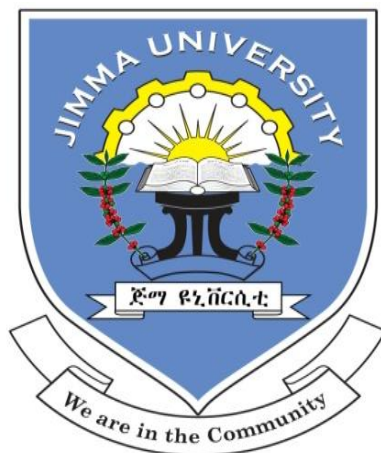


JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



A THESIS REPORT

ON

**EXTRACTION, PREPARATION AND APPLICATION OF DYES FROM
Persicaria lapathifolia (FLOWERS AND ROOTS) AS SENSITIZERS FOR
DYE SENSITIZED SOLAR CELL**

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DYE SENSITIZED SOLAR CELL

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ABBREVIATIONS

CE	-----	Counter Electrode
CV	-----	Cyclic Voltsmmetry
Cy	-----	Cyanidin
Dp	-----	Delphinidin
DSSC	-----	Dye-Sensitized Solar Cell
Equ.	-----	Equation
FF	-----	Fill Factor
FTO	-----	Fluorine doped Tin Oxide
HOMO	-----	Highest Occupied Molecular Orbital
hr	-----	hour
ITO	-----	Indium doped Tin Oxide
IPCE	-----	Incident Photon to Current Conversion Efficiency
LUMO	-----	Lowest Unoccupied Molecular Orbital
Mv	-----	Malvidin
PEG	-----	Poly Ethylene Glycol
Pg	-----	Pelargonidin
PGE	-----	Pencil Graphite Electrode
Pn	-----	Peonidin
<i>P.l.</i>	-----	<i>Persicaria lapathifolia</i>
Pt	-----	Petunidin
P-V	-----	Power Voltage
R.E	-----	Reference Electrode
TBA	-----	Tetra Butyl Ammonium
TBP	-----	Tertiary Butyl Pyridine
TCO	-----	Transparent Conducting Oxide
TFPV	-----	Thin Film Photo Voltaic cell
TFSC	-----	Thin-Film Solar Cell
WE	-----	Working Electrode

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ABSTRACT

Dye sensitized solar cell (DSSC) is a photovoltaic device that converts light energy into electrical energy that is composed of dyed working electrode, electrolyte and counter electrode. The dye molecules adsorbed on TiO₂ surface are responsible for light absorption. Accordingly, as this study was aimed to extract, prepare and use dyes from flowers and roots of *Persicaria lapathifolia* as sensitizer for dye sensitized solar cell (DSSC); two DSSCs one for flower extract and one for root extract were prepared by Doctor's Blade method. These dyes showed good absorption in visible range and optically responsible compounds were phytochemically screened. The electrochemical behavior and optical absorption property of flower and roots dyes were estimated by cyclic voltammetry and spectrophotometry (UV-Vis) respectively. As a result HOMO of flower extract dye was 0.322 eV and LUMO was -1.538 eV. While HOMO of root extract dye was 0.306 eV and LUMO of root was -1.594 eV. I-V and P-V curves were plotted by using Extech Multimeter, fluorescent lamp and electrical circuit made from resistors connected on wood board. Finally based on characterization of DSSC made from flower with efficiency ($\eta=2.49\%$) whereas the DSSC made from root with efficiency ($\eta= 1.93\%$) were obtained. Therefore, according to this work flower dye sensitized DSSC is more efficient than root dye sensitized DSSC. However, this work needs improvement to be scaled up based on recommendation set and seeks further study, too.

Key words: DSSC; dyes; Persicaria lapathifolia; Doctor's Blade method; cell efficiency

CHAPTER ONE

1. INTRODUCTION

1.1 Back ground of the study

Dye sensitized solar cell (DSSC) is a photovoltaic device or material that converts incident photon energy of solar radiation in to usable electrical energy through the generation and subsequent collection of electron-hole pairs [1]. It is made up of anodic /negative terminal/ metal oxide semiconductor, sensitizing dye, electrolyte solution and cathodic /positive terminal/ counter electrode.

Among the wide band gap nano-crystalline metallic oxide semiconductors titanium dioxide, TiO_2 , has been mostly used in the DSSC application for it has widely remarkable stability in physical, chemical, non-toxicity, optical and electrical properties [2]. TiO_2 is also a favorite semiconductor for its conduction band edge lies to some extent below the excited state energy level of mostly various dyes, which is a necessary condition for efficient electron injection and has high dielectric constant that provides effective electrostatic shielding to the injected electron not to make glance with the oxidized dye molecule, thus prevents separated electron from recombination before reduction of the dye by the redox electrolyte [3, 4]. So as to be working electrode TiO_2 film is pasted on conductive glass, sintered and immersed in the natural dye solution to anchor a monolayer of the dye on the surface of mesoporous TiO_2 to absorb visible light [4].

The natural dyes that we use for sensitization are mainly found in flowers, leaves, roots, fruits and other parts of plants that can be extracted by simple procedures [5, 6]. Due to their plenty of availability with uncomplicated extraction process they have been enthusiastically studied, estimated as low-cost per watt and promising sensitizers for DSSCs [7]. As consequence, currently the research on the dye extracted from natural sources as a photo-sensitizer for DSSC has gained a great attention in the world due to their vast absorption coefficient, high light-harvesting efficiency, low investment cost, easy preparation and environmentally benign. In addition, the dyes ought to have the subsequent essential properties: a wide-ranging absorption response in the visible-light region, large amount of the pigments (such as flavonoids, anthocyanin, chlorophyll, etc) groups, strong chemical stability, interestingly comprehensive

compatibility with solvent as well as semiconductor and a short-chain molecular configuration [8].

The anthocyanin and chlorophyll are some of coloring components found in fruits, flowers, roots and leaves of plants responsible for several colors in the red–blue range and green respectively. They have anchoring groups, carbonyl and hydroxyl, that make attachment to the surface of a porous TiO₂ film and allow electron injection. This paves the way to the electron transfer from the pigments, (anthocyanin and chlorophyll), molecule to the conduction band of TiO₂ and the oxidized species regenerated by accepting electron from electrolyte solution [9].

The electrolyte is used to transport the electrons back to the oxidized dye molecules in order to the dye molecule regenerate and rebirth at its origin of ground state to maintain the system recycling for long expected time. After donating electron to the oxidized dye molecule an oxidant of electrolyte becomes oxidized. The oxidized electrolyte redox couple reduced at counter electrode and becomes regenerated. The most common electrolyte consists of redox couple (like, I⁻/I₃⁻) in organic solvent such as acetonitrile (ACN) [10].

The counter electrode in DSSCs is the activated plain of FTO by carbon or graphite to reduce tri-iodide to iodide as catalyst serves as redox couple regeneration reaction. It is accounted as positive terminal electrode that can be prepared by coating conductive side of FTO glass with graphite rode or soft pencil to form a light carbon film on the entire expected conductive side of the plate and it becomes ready for cell assembling [10, 11].

The full structure of DSSC is an assembly or sandwich of anodic working electrode, an electrolyte solution and a cathodic counter electrode. Finally the prepared cell is exposed to light source, the operations start and characterization follows [11].

Among the components of DSSC working electrode is the main for it hosts dye molecule which is a major part of research issue. Since the role of the absorption of visible light and the conversion of photon energy into electricity is played by the dye, much attention should be paid in the exploration based on light absorbing chemical constituents and analysis of effective sensitizer [12]. For instance, due to their intense charge transfer absorption in the whole visible range, transition metal coordination compounds (ruthenium polypyridyl complexes) based dyes are generally used as the effective sensitizers although they have complicated synthesis process, are environment pollutant, limited in amount and high in cost[13, 14]. Hence, natural

dyes are chosen as profitable to be the best alternative as they can be used for the same purpose with acceptable efficiency [15-17].

Natural dye as sensitizer for DSSC has been preferred due to their easily processing and more of that complete biodegradability so far as popular subject of new research area. Alhamed et al. reported homemade DSSC prepared using natural dyes extracted from raspberries, shami-berries, grapes, hibiscus and chlorophyll [18] similarly Lai et al. applied *rhoeo spathacea* in DSSC as a dye sensitizer [19] are some examples of natural dyes that have been used as DSSC dye sensitizers and still the effort is going on for search of plants that yield high quality and efficient natural dyes. However, dyes extracted from *Persicaria lapathifolia* flowers and roots yet not tested as sensitizer for DSSC. Consequently, in this work, natural dye extracts from *Persicaria lapathifolia* flowers and roots were used as photo sensitizer in DSSC and their effects on the solar cell parameters have been observed.

1.2 Statement of the problems

The fast grow of world population with development scramble increases the demand of energy more than the traditional energy supply trend covers [20]. To overcome this problem the investigation of modern and sophisticated renewable alternative energy source ought to be designed/invented/ such as solar system that built up from solar cells. The first ranker solar cell from silicon wafer as semiconductor is expensive due to its high production cost per watt although highly efficient. Due to this reason the end users are expected to expend more money to buy this device for their energy consumption at home or commercial usage and it has been out of the buying capacity of the community who have low income.

The another option that has been modeled to solve the above problem is the thin film solar cells called second generation solar cell are Cadmium telluride (CdTe), Copper indium gallium diselenide (CIGSe₂) and amorphous silicon (a-Si) have also remarkably less efficiency in comparison to silicon element based solar cell and associated with toxicity has still limitation could not satisfy the demand [21]. Owing to these, another suitable model of solar cell or dye sensitized solar cell fabrication has been developed by using organic dye extracted from natural plants as photo-sensitizer attracted the attention of many research works for its availability, non-toxicity, complete biodegradability and temperature compatibility [22].

Although many researchers have worked on various plants extracted dye sensitized solar cell fabrication, no attempts have been made for the dye extracted from *Persicaria lapathifolia*

flowers and roots based DSSC, yet. The *Persicaria lapathifolia* is rich in flavonoids, suitable phytochemical, for DSSC fabrication and the dyes were extracted with polar solvents. Therefore, extracting dyes from *Persicaria lapathifolia* flowers and roots are important and valuable as light sensitizer for DSSC fabrication. Consequently, this work was designed to focus on the *Persicaria lapathifolia* flowers and roots extracted dye as sensitizers for TiO₂ based dye-sensitized solar cell by answering upcoming questions;

- ❖ What dyes could be extracted from *Persicaria lapathifolia* flowers and roots; had effect on DSSC fabrication?
- ❖ What would the absorption capacity of the extracted dyes be?
- ❖ What would the efficiency of these dyes sensitized solar cell be?

1.3. Objective of the study

1.3.1 General objective

The main objective of this study was to extract, prepare and use dyes from *Persicaria lapathifolia* flowers and roots as sensitizers for TiO₂ based dye-sensitized solar cell.

1.3.2 Specific objectives

The specific objectives of this study were;

- ❖ To extract natural dyes from flowers and roots of *Persicaria lapathifolia* and screen phytochemicals.
- ❖ To determine optical properties of extracted dyes.
- ❖ To determine electrochemical energy performance of extracted dyes.
- ❖ To prepare extracted dyes sensitized DSSCs.
- ❖ To characterize extracted dyes sensitized DSSCs.

1.4 Significance of the study

Since the demand of global energy consumption has been increasing year after year the environmental pollution free, cost effective, reliable, easily adaptive, attractive and durable alternative energy technology fabrication and supply is a key issue of the contemporary world.

The natural dye-sensitized solar cells (DSSC) is one of the special solution to secure the energy sector problem and emerged as a new class of energy conversion devices with simple manufacturing procedures. The natural dye is different from artificial synthetic dye for it is easily available, easy to prepare, low cost, non-toxic, environmental friendly and fully

biodegradable [23]. Therefore, this study maximizes the attitude of new technology development and the result is one of the research input for the next other researchers in *Persicaria lapathifolia* related works. Another benefits are it creates awareness about *Persicaria lapathifolia* in application of DSSC preparation, is input of one of investment potential for energy sector interested investors and promotion of suitable energy source for end users

CHAPTER -TWO

2. REVIEW OF RELATED LITERATURE

2.1 Solar cell /electricity/

A light sensitive material that converts solar energy into electrical energy is known as solar cell. Many unified solar cells with respect to sizing and connection preferences arranged into solar panel and the array of panels give a system which provides solar electricity [24]. The solar electricity is an emerging technology today and anticipated for small scale up to centralized megawatt scale power plants [25]. However, to be accessible in large extent to generate electricity from the sun light radiation it has loads of features over other energy generation techniques. For instance, high cost of solar cells per watt has been a significant hindrance for the achievement of the solar electricity in a large scale [26]. Therefore, to be solution for this problem the development of new materials and technology is important to reduce this cost. Lots of researches have been recently going on nanotechnology development in order to exhibit high efficient solar energy conversion with relatively reduced costs per watt of solar cell as well as environmentally benign [27].

2.2 Types of solar cells

2.2.1 Crystalline silicon solar cells

The most widely dominant solar cells have been produced all over world from silicon(Si) semiconductor material/wafer/ as it is the second most abundant element in earth`s crust [28]. To produce a solar cell, the semiconductor has to be contaminated or "doped". "Doping" is the deliberate introduction of chemical elements, in which one can obtain a excess of either positive charge carriers (p-conducting semiconductor layer) or negative charge carriers (n-conducting semiconductor layer) from the semiconductor material [29].

The crystalline silicon is usually referred to as the first generation photovoltaic technology. It can be categorized as mono; due to the regularly ordred crystal structure which is obtained by a very sluggish growth of crystals that makes this the type of silicon which has the most consistent and predictable behavior of cells from the same wafer that makes it is the most expensive type of silicon and polycrystalline; has a dissimilar structure with fast growing that makes to have many crystals within the structure and the orientation of the crystals is random.

In polycrystalline the crystals congregate in a 'grain boundary' and these boundaries reduce the efficiency of silicon when compared to monocryalline. Due to high efficiency today the silicon solar cells dominate the photovoltaic (PV) market although has high cost [30]. The processing of crystalline silicon wafers requires high-level semiconductor technology, and owing to this it is expensive and very high capital demanding [31]. This loads the cost of the photovoltaic system to become high as cost of processed silicon wafers contribute to fifty percent of the total manufacturing cost of the module [32].

2.2.2 Thin film solar cells

A solar cell that is made from materials such as amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium gallium diselenide (CIGSe₂), which are called thin because their working electrode encompasses much thinner films (~1 μm) than that of the first generation (~350 μm) called thin film crystalline silicon, also known as second generation solar cell [33]. It is manufactured by depositing one or more thin layers (thin film) of photovoltaic material on a substrate to be called as thin-film solar cell (TFSC), a thin-film photovoltaic cell (TFPV) [34]. The main driving force that the thin film solar cells to be developed are the demand of reduction of complicated and difficult fabrication processing as well as lower manufacturing costs [35].

2.2.3. Dye sensitized solar cells, DSSC

The dye-sensitized solar cell (DSSC) is the third generation of photovoltaic devices for the conversion of solar energy into electric energy was firstly developed by M. Grätzel, in 1991 [36]. The DSSC is produced by the application of dyes on wide band-gap semiconductors such as TiO₂ as photo-sensitizer. This sensitization is due to the dye's absorption capacity of ample visible light spectrum as semiconductor by itself couldn't for it has large band gap than electron be able to jump through up [37]. DSSCs are low cost solar cells because of cheaper materials and relatively ease of the fabrication processes [38]. The metal oxide, TiO₂, has been fruitfully used as photo-anode when a dye is adsorbed on the surface of the porous layer of the semiconductor [39].

2.2.3.1 Inorganic dye sensitized solar cell

Dyes that are required to prepare DSSC usually consist of polypyridyl complexes of some transition metal, ruthenium or osmium. Ruthenium polypyridyl complexes are used as

successful sensitizers due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer (MLCT). However, has complicated synthesis process, expensive and environmentally unfriendly [40].

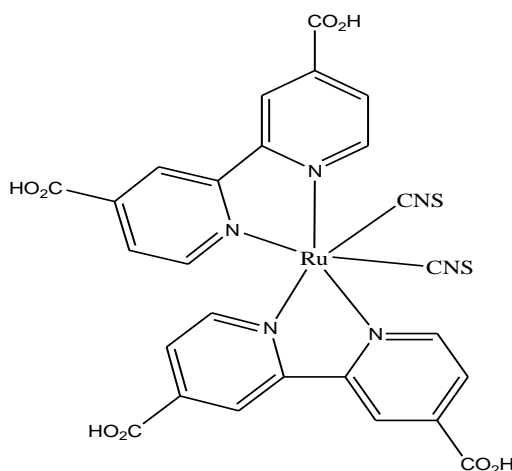


Figure 1: N3, red dye.

2.2.3.2 Natural dye sensitized solar cell

The natural pigments/dyes can be extracted from fruits, leaves, flowers, roots and vegetables being responsible for various colors are engaged in DSSC. These plant pigments exhibit electronic structure that interacts with sunlight and alters the wavelengths that are either transmitted or reflected by the plant tissue. This process leads to the occurrence of plant pigmentation and each pigment is described from the wavelength of maximum absorbance (λ_{\max}) and the color perceived by humans. Pigments for natural dyes include chlorophyll, carotenoid, flavonoid and anthocyanin that are relatively easy to extract from natural products when compared to synthetic dyes. Such pigments have been comprehensively investigated as photosensitizing dyes are to convert solar energy into electrical energy since they have high absorbing capacity within UV-Vis range and economically viable as well as have significant environmental benefit [41].

The use of natural stuff as sensitizing dye for the energy conversion device/solar cell/ is very fascinating due to economical viability since it is inexpensive for they do not contain noble metals like Ru, Pt, and Os. Furthermore, wide varieties of structures that can be obtained provide possibilities for molecular design and allow easy control of their absorption spectra. The organic dyes with the general structure of Donor (D)- conjugation bridge(π)- acceptor (A) integrated have high molar absorption coefficients relative to those of Ru-complex sensitizers

owing to intramolecular π - π^* transitions. Consequently, enhance the photovoltaic performance of DSSC based on organic dye sensitizers [42].

Due to the incident irradiance of visible light falls on the DSSCs there is charge separation with kinetic competition mimic to natural photosynthesis [43], as solar cell charge separation considered via the movement of charge carriers or drift currents in the p-n junction [44]. Besides, the dye in a DSSC or photo electrochemical particle substitutes for the chlorophylls, the nano-structured semiconductor layer substitutes for the nicotinamide adenine dinucleotide phosphate and carbon dioxide acts as the electron acceptor. Furthermore, the electrolyte substitutes for the water, whereas oxygen acts as the electron donor and oxidation product [45]. Since the development of concept of DSSC by M. Gratzel and his co-workers in the year 1991 many works have been done by various researchers up to now. However, the technology still needs improvement for its low efficiency and extra research works are expected unto the efficiency problem becomes solved [46]. In order to be the reference point to the current work some of the works that were done by various workers has been listed in the table 1, as follows;

Table 1: Different natural dyes extracted from leaves, seeds, flowers, fruits, vegetables and tree barks to sensitize DSSCs [47, 48].

No	Dye solution plant source/	Semiconductor	Electrolyte	Pigment used	λ_{max} (nm)	Jsc (mA cm ⁻²)	Voc (V)	FF	η (%)
1	Spinach (<i>Spinacia oleracea</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Chlorophyll	437	0.47	0.55	0.51	0.13
2	Redcabbage (<i>Brassica olercea</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Anthocyanin	537	0.50	0.37	0.54	0.13
3	Red onion (<i>Allium cepa</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Anthocyanin	532	0.51	0.44	0.48	0.14
4	Botuje (<i>Jathopha curcas</i> L.)	TiO ₂	I ⁻ /I ₃ ⁻	Flavonoid	400	0.69	0.05	0.87	0.12
5	Shiso(<i>Perilla frutescens</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Chlorophyll	440&600	3.56	0.55	0.51	1.01
6	<i>Ficus retusa</i>	TiO ₂	I ⁻ /I ₃ ⁻	Chlorophyll	670	7.85	0.52	0.29	1.18
7	Sumac(<i>Rhustyphina</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Anthocyanin	650	0.93	0.394	0.41	1.5
8	Henna (<i>Lawsonia inermis</i>)	TiO ₂	I ⁻ /I ₃ ⁻	Anthocyanin	518	1.87	0.61	0.58	0.66

2.2.3.3. Components of the dye-sensitized solar cell

A. Substrates

The electrodes of the typical DSSC are made from transparent conducting oxide (TCO) covered on glass substrates, where the cell is sandwiched between. Fluorine doped tin oxide ($\text{SnO}_2:\text{F}$), FTO and indium doped tin oxide ($\text{In}_2\text{O}_3:\text{ITO}$) are commonly used TCOs in thin film photovoltaic cells technology. Since FTO is stable at elevated temperatures it has been preferred as the best TCO for DSSCs. The conducting coat of the substrate works as a current collector and the substrate material itself as both a supportive structure to the cell and as a sealing layer between the cell and the ambient air [49].

B. Titanium dioxide, TiO_2 , semiconductor

TiO_2 is a wide band gap ($E_g = 3.2$ eV) metallic oxide semiconductor. It is cheap to be produced and the preparation of particles of very small size is moderately easy [50]. The TiO_2 has three crystallite morphological structures: anatase, rutile and brookite. Among these brookite is very difficult to obtain. For rutile absorbs visible light near UV-region the band gap excitations lead to generate holes and this causes long term instability loads of the solar cell. Anatase is a dominant allotropic at low temperatures and is preferred over other polymorphs for solar cell applications due to its higher electron mobility, high refractive index, high dielectric constant and lower density. Rutile absorbs only 4% of the incoming light near-UV region, and band gap excitation generates holes that act as strong oxidants that reducing the long-term stability of the dye sensitized solar cells. The activity of the rutile phase as a photo catalyst is generally very poor. The third crystalline form of TiO_2 , brookite, is difficult to produce and is therefore not of practical interest for the DSSC. The band-gaps of the crystalline forms are 3.2 eV for anatase at the absorption edge of 388 nm and 3.0 eV for rutile at the absorption edge of 413 nm [51].

C. Sensitizing dyes

To attain highly appreciable light-to-energy conversion efficiency in a DSSC, the properties of the dye molecule that are attached to the semiconductor particle surface as back bone are important [52]. Such enviable properties may be summarized as:

- ❖ **Interfacial properties:** excellent adsorption to the semiconductor surface
- ❖ **Practical properties:** e.g. unsparingly solubility to the solvent used in the dye impregnation.

- ❖ **Stability:** the adsorbed dye molecule should be long life stable in the working environment at exposure to natural daylight.
- ❖ **Kinetics:** the path of electron injection from the excited state of the dye to the conduction band of the semiconductor ought to be fast enough to exceed competing unnecessary relaxation and reaction pathways.
- ❖ **Absorption:** the dye must absorb light at longer wave length about 920 nanometers, i.e. the energy of the excited state of the molecule should be about 1.35eV above the electronic ground state corresponding to the ideal band gap of a single band gap solar cell.
- ❖ **Energetic:** to minimize energy losses and to maximize the photo-voltage, the excited state of the adsorbed dye molecule should be only slightly above the conduction band edge of the TiO₂, but yet above enough to present an energetic driving force for the electron injection process. For the same reason, the ground state of the molecule should be only slightly below the redox potential of the electrolyte [53].

D. Electrolytes

The electrolyte is used to transport the electrons back to the oxidized dye molecules in order for the dye molecule to regenerate and rebirth at its origin of ground state to maintain the system recycling. Currently three different kinds of electrolytes have been used in real DSSCs, (i) the most common electrolyte is I^-/I_3^- in organic solvents, such as acetonitrile. Occasionally lithium ion is added to smooth the progress of electron transport. This kind of electrolyte is good for ion diffusion and infiltrate well with TiO₂ film, keeping highest efficiency of all DSSCs. But limited long-term stability due to volatilization of liquid hinders its wide use. (ii) Inorganic ionic liquids made of salts or salt mixture. It looks like solid while it has properties of liquid and it performs well in conductivity. But after a long period of time, its efficiency declines. (iii) Solid electrolyte, such as CuI, CuSCN. For CuI, its instability and crystallization makes it hard to fill in the porous TiO₂ films. However, in this work deliberately it has been decided to use electrolyte consisting of redox couple (like I^-/I_3^-) in a solvent such as acetonitrile (ACN). The performance is feasible with acetonitrile due to lower viscosity. The ultimate characteristics of the redox couple for the DSSC electrolyte are [54, 55]:

- ❖ redox potential thermodynamically (energetically) favorable with regard to the redox potential of the dye to elevate cell voltage/ potential;

- ❖ complete solubility to the solvent to guarantee high concentration of charge carriers in the electrolyte;
- ❖ high diffusion coefficients in the involved solvent to facilitate efficient mass transport;
- ❖ absence of significant spectral interference in the visible region not to intervene absorption of incident light in the electrolyte;
- ❖ The best stability of both the reduced and oxidized forms of the couple to sustain long operating life;
- ❖ Actively reversible couple to smooth the progress of fast electron transfer kinetics; chemically inert toward all other components in the DSSC [55, 56].

E. Counter electrode catalyst

The counter electrode in DSSCs is the activated plain of FTO by carbon to reduce tri-iodide to iodide as catalyst [57, 58]. The counter electrode as positive terminal can be prepared by coating conductive side of FTO glass with graphite rod or soft pencil to form a light carbon film on the entire conductive side of the plate. Any loose graphite particles should be gently removed. This thin carbon layer serves as a catalyst for the tri-iodide-to-iodide regeneration reaction. For lifelong the carbon-coated counter electrode should be annealed at 60°C for a few minutes , washed with ethanol and gently blotted/ stained/ to dry before the device is assembled [59].

F. Sealing of dye-sensitized solar cell

Air tight sealing is very essential to achieve stable solar cells for longevity. The most common DSSC sealing material is thermoplastic. A thermoplastic frame helps to connect the working electrode /WE/ and counter electrode /CE/ together to confirm a fixed separation between the two electrodes [60].

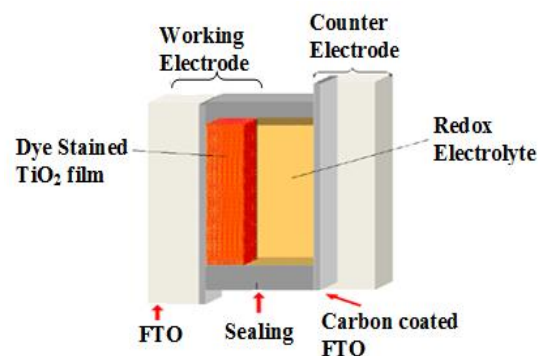


Figure 2: Sealing feature of dye-sensitized solar cell [60].

A proper sealing of DSSC should at least be:

- ✓ Leakage-free to the electrolyte environment and impermeable to external ambient oxygen and water vapor.
- ✓ Chemically inert towards the electrolyte and other species of cell components.
- ✓ Devoted well to the glass substrate and transparent conduction oxide coating [61].

2.2.3.4. Operating principle

DSSC is mimic to natural photosynthesis by using a dye as the light harvester to provide excited electrons, TiO_2 replacing carbon dioxide as the electron acceptor, iodide/ triiodide (I^-/I_3^-) replacing water and oxygen as the electron donor and oxidation product and a multilayer structure (similar to the thylakoid membrane) to enhance both the light absorption and electron collection efficiency. The light-driven electrochemical process in DSSC is regenerative and the working voltage produced by the device is the difference between the chemical potential of the TiO_2 (Fermi level) and the redox potential of the mediator (I^-/I_3^-). The second process characteristically requires a catalytic amount of counter electrode, for instance carbon /graphite/ on the cathode surface. The process control is maintained by kinetic competition. In optimized way a favorable kinetic balance assures that loss mechanisms such as the thermalization of the dye excited state and other recombination processes are largely suppressed [62].

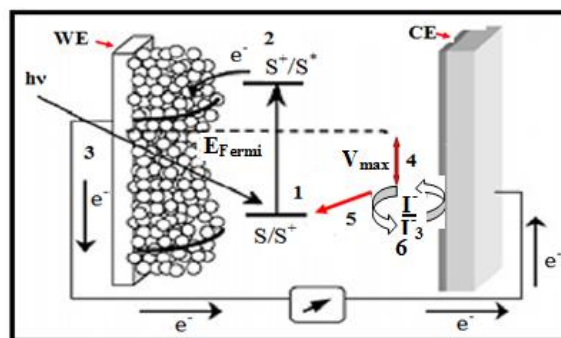
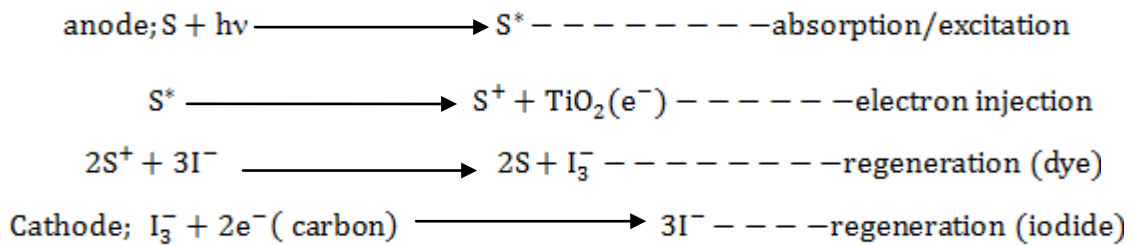


Figure 3: Complete operating cycle of DSSC [62].

1. ground state and oxidized state of dye molecule,
2. excited and oxidized state of dye molecule,
3. flow of electron through external circuit,
4. maximum voltage, V_{oc} , difference between E_{fermi} level and reduction potential of the redox (I^-/I_3^-) couple.
5. regeneration of dye molecule,
6. regeneration of redox couple,

The operating cycle can be summarized in chemical reaction terminology as,



In the DSSC three major operating phenomena takes place.

- Light absorption.
- Charge separation.
- Charge collection.

The competence of a solar cell depends on the efficiency of each of these elements and can be maximized by the materials selection with appropriate cell design.

2.2.3.5. Parameters for solar cells characterization

The essential parameters of the DSSC are short circuit current (I_{sc}), open circuit voltage (V_{oc}), optimum voltage (V_m), optimum current (I_m), fill factor (FF) and efficiency (η), Incident Photon to Current conversion Efficiency (IPCE) [63].

I. Short circuit current, I_{sc}

When the output voltage drops to zero, the cell is said to be short circuited. The short circuit current is equivalent to the exact number of photons converted to hole-electron pairs. The I_{sc} depends on the breadth of the electrode, diffusion electrolytes, the adsorbed dye molecule, dipping time, temperature of the cell and dye loading.

II. Open circuit voltage, V_{oc}

When the output current drops down near zero, the cell is called open circuited and the voltage of the cell is known as the open circuit voltage, which leans on wide band gap of semiconductors, redox potential and the ground state of the dye molecule.

III. Optimum voltage, V_m

V_m is optimum voltage that operates at position where the DSSC output power is maximum. It depends on cohesive bonds between the dye molecule to TiO_2 film, dying temperature and time duration.

IV. Optimum current, I_m

I_m is optimum current that operates at point where the DSSC output power is maximum. It depends on the intensity of incident light and links between material interfaces.

V. Fill factor, FF

The fill factor is an essential part of the efficiency of the cell. High V_{oc} and I_{sc} are crucial for high efficiencies, but paired with a low fill factor, the overall efficiency of the cell will remain low. The ratio of peak output power $V_m I_m$ to $V_{oc} I_{sc}$ is called the fill factor (FF) of a solar cell.

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} = \frac{P_m}{I_{sc} V_{oc}} \text{-----} 1$$

P_m , is maximum power, $V_m I_m$

VI. Efficiency, η

The energy conversion of a solar cell is defined as the ratio of the output power of the cell to incident irradiance. Maximum efficiency is attained when power transmitted to the load is P_{max} . The maximum efficiency can be calculated from the J-V curve according to the relation

$$\eta = \frac{I_m V_m}{P_{light}} = FF \frac{I_{sc} V_{oc}}{P_{light}} \text{-----} 2$$

$P(light)$ is the energy of the incident light falls on the a solar cell and is obtained when the light intensities of the whole spectral range are integrated.

VII. Incident photon to current efficiency (IPCE)

The incident photon-to-current conversion efficiency (IPCE) can be expressed as “external quantum efficiency” (EQE), is an essential attribute of a device [64, 65]. By using the same architecture of device we are able to compare the light-harvesting efficiency of sensitizers [66].

IPCE is boldly defined as the number of electrons generated in the external circuit by incident photo-light divided by the number of incident photons as a function of excitation wavelength as;

$$\text{IPCE}(\lambda) = \frac{\text{photo current density}}{\text{Wavelength} \times \text{Photon flux}} \text{-----} 3$$

$$= \text{L. H. E}(\lambda) \cdot \varphi_{inj} \cdot \eta_{col} \text{-----} 4$$

Where, $\text{LHE}(\lambda)$ is the light-harvesting efficiency at wavelength, λ ; φ_{inj} is the quantum yield for electron injection from the excited sensitizer in the conduction band of the TiO_2 , η_{coll} is the efficiency for the collection of electrons [67].

Electrical power is generated by illumination at 1.5 AM achieved mainly by the virtue of prepared DSSC to produce voltage over an external load and current through the load at the same time. Generally, DSSC is characterized by current density-voltage (J-V) curve and power-voltage (P-V) curve of the cell as shown in figure 4 [68].

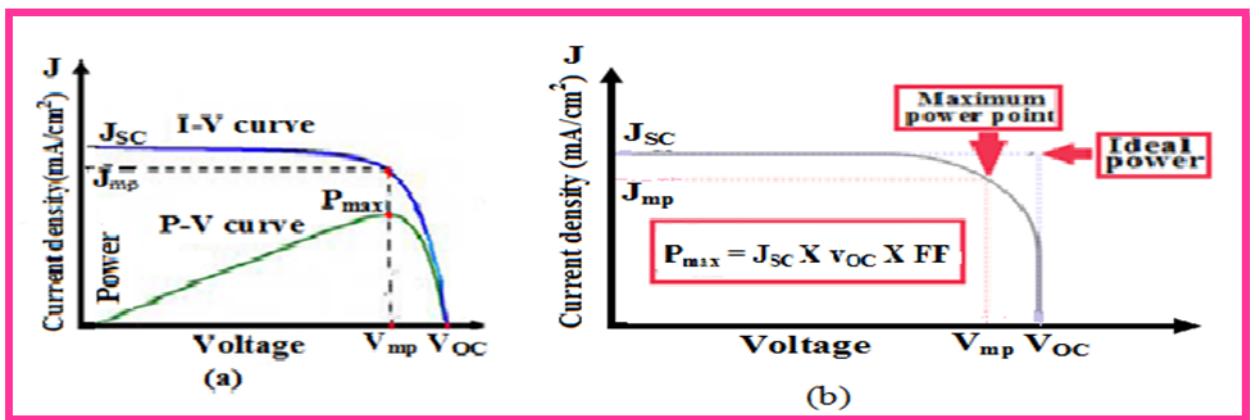


Figure 4: (a) Current-voltage (I-V) curve and power (P-V) curve of the cell and (b) illustrates the performance of DSSCs and the solar power (P) can be calculated by the equation: $P=IV$ [68].

As we can see from above Figure4, if the cell is become short circuited under illumination, we might have the maximum current (short circuit I_{SC}) or short circuit current density (J_{SC}) generation, as well as under open circuit situation there could have no current flow and the voltage (open circuit voltage, V_{OC}) is at its maximum.

$$P_{max} = V_m I_m = V_m J_m A_{cell} \text{-----} 5$$

Where:

I_{mp} = the current at the maximum power output

J_{mp} = the current density at the maximum power output

V_{mp} = the voltage at the maximum power output

A_{cell} = the illuminated cell area

2.2.3.6 Brief introduction on phytochemicals classes commonly applied in preparation of DSSC

In plants the naturally occurring chemical compounds are phytochemicals and significantly expended in DSSC preparation. Among them polyphenols, anthocyanin, flavonoids, quinone, anthraquinone, coumarines, chlorophyll, carotinoid, etc. are the most commonly used pigments. Therefore, phytochemical screening of intended plant extract is an important attributive technique that helps to detect the availability of interested phytochemicals and helps to make unbiased decision to work with supposed plants. Generally, the phytochemical tests for the chemical compounds that have practical relevance in DSSC applications can be performed with liquid plants extracts by using known standard methods as described in Table 2 [69].

Table 2: Protocols of Phytochemical screening

Phytochemicals	Test	Indicator	Ref.
Phenol	a) 1ml extract + 2 ml of distilled water +10% FeCl ₃ . b) Extract + 10% sodium hydroxide.	b) Blue or green colour a) Blue colour	[69]
Anthocyanin	a) Extract + conc. sulphuric acid. b) Small amount of extract + 2N NaOH.	b) Yellowish orange. b) Blue-green color	
Quinones	1 ml of extract + 1 ml conc. H ₂ SO ₄ .	Red color.	
Cuomarines	1 ml of 10% NaOH + 1 ml of extract.	Yellow color.	
Anthraquinones	1ml extract + few drops of 10% NH ₃ .	Pink color precipitate.	
Flavonoids	a) 1 ml extract + few drops of NaOH, b) 1 ml extract + few drops of NaOH + few drops of dilute acid.	-An intense yellow color. -Colorless appearance.	
Carotenoids	Extract + chloroform + drops of conc. H ₂ SO ₄ .	Deep-blue colored layers	

A. Flavonoids

Chemically, flavonoids have the general structure of a 15-carbon skeleton, may be abbreviated C₆-C₃-C₆, which consists of two phenyl rings and a heterocyclic ring that distinguishes one

flavonoid compound from the other. In case of flavonoids, the charge transfer transitions from HOMO to LUMO require lesser energy, energizing the pigment molecules by visible light, leading to a broad absorption band in the visible region. This flavonoid instantly adsorbed to the surface of TiO_2 by displacing an OH^- counter ion from the Ti (IV) site that combines with a proton which is donated by the flavonoid [70].

B. Chlorophylls

Chlorophylls belong to natural photosynthetic pigments that are responsible for plants to bear green color. The two main categories of chlorophylls are chlorophyll 'a' and chlorophyll 'b'. Chlorophylls and their derivatives are employed as sensitizers in DSSC due to their tendency to absorb blue and red light. The most efficient is the derivative of chlorophyll 'a' (methyl trans-32-carboxy-pyropheophorbide). The absorbance spectrum of chlorophyll 'b' indicates a typical blue tinge and has a red shift when compared to chlorophyll 'a' [71]. Chemical structure of Chlorophyll 'a' and Chlorophyll 'b' are shown below.

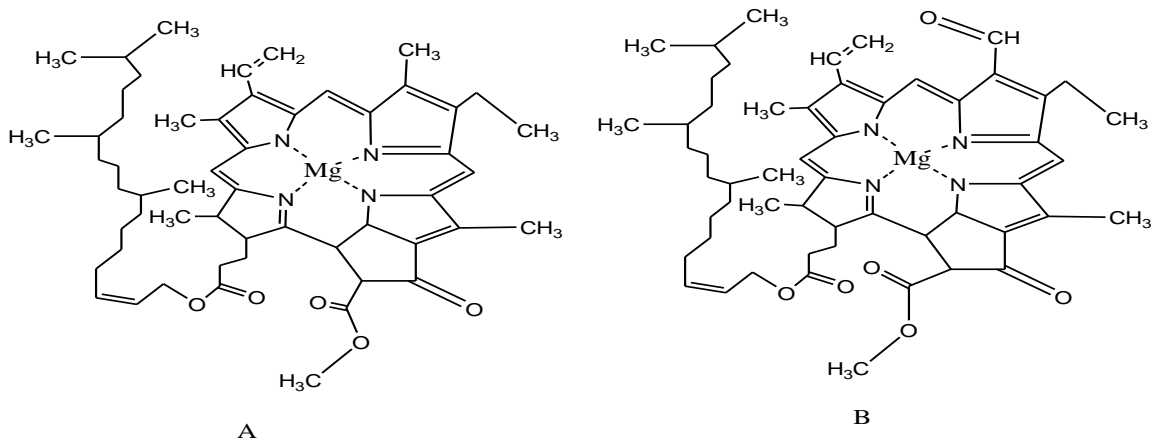


Figure 5: Molecular structure of chlorophyll a (A) and chlorophyll b (B).

C. Anthocyanins

Anthocyanins are responsible for existence of attractive colors from scarlet to blue of flowers, fruits, leaves, roots,... etc and are even identified in mosses and ferns. Anthocyanins are also responsible for modifying the quantity and quality of light that is incident on the chloroplasts. Anthocyanin molecules have carbonyl and hydroxyl groups bound to the surface of TiO_2 semiconductor, which helps in excitation and transfer of electrons from the anthocyanin molecules to the conduction band of porous TiO_2 film [72]. The bonding process between the functional groups such as carbonyl and hydroxyl groups with TiO_2 surface is shown below.

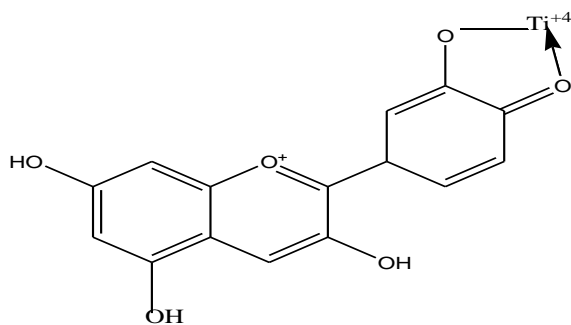


Figure 6: The basic molecular structure of anthocyanin and the binding between anthocyanin molecule and TiO_2 particles [72].

From different plants sourced anthocyanin can absorb visible light at different wavelength as natural photo-sensitizer has different absorption peaks. For examples, the absorption peaks of anthocyanin from beetroot dye are at 478nm and 540nm, grapes dye at 529nm, raspberry shows two absorption peaks at 207 nm and 279 nm, and the absorption peaks of anthocyanin extracted from black plum are at 553 nm and 662 nm and the dye extracted from mangosteen absorbs at 378 nm[73].

Structurally, anthocyanin stems from the main structure of anthocyanidin that comprises benzopyran core [benzoyl ring (A), pyran ring (C)], a phenolic ring (ring B) attached to its (2-position and a sugar moiety mainly at its 3-position in the C-ring. 90% of all naturally occurring anthocyanins are based on six aglycones differing in their B-ring substitution pattern: cyanidin (Cy) about 50%, delphinidin (Dp), pelargonidin (Pg) and peonidin (Pn) about 12% each and petunidin (Pt), malvidin (Mv) about 7% each [74].

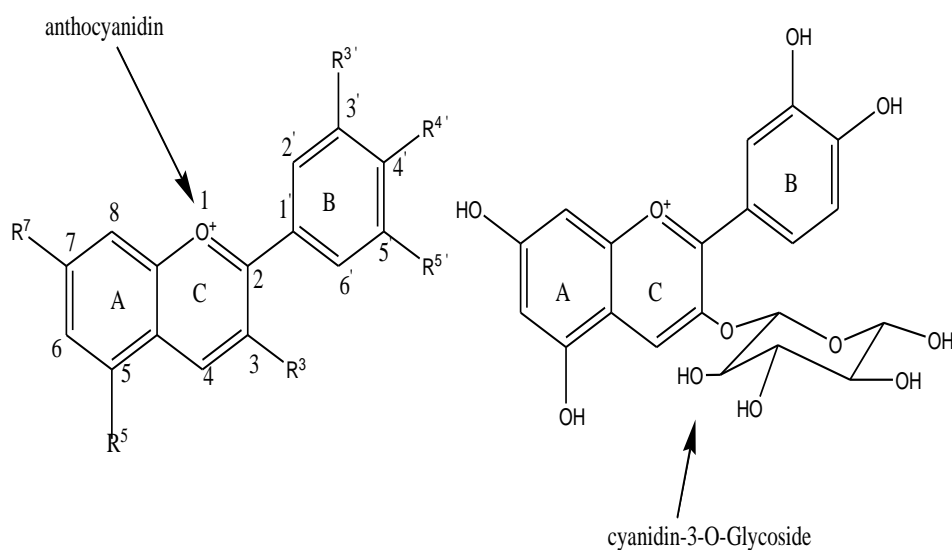


Figure 7: Structure of anthocyanidin back bone and anthocyanin [74].

Table 3 details of possible anthocyanins [74].

	symbols	R ^{3'}	R ^{4'}	R ^{5'}	R ³	R ⁵	R ⁶	R ⁷
Cyaniding	Cy	OH	OH	H	OH	OH	H	OH
Delphinidin	Dp	OH	OH	OH	OH	OH	H	OH
Malvidin	Mv	OCH ₃	OH	OCH ₃	OH	OH	H	OH
Pelargonidin	Pg	H	OH	H	OH	OH	H	OH
Peonidin	Pn	OCH ₃	OH	H	OH	OH	H	OH
petunidin	Pt	OH	OH	OCH ₃	OH	OH	H	OH

Anthocyanin can be existed in various chemical forms with respect to different pH ranges. At pH=3 or below, the flavylium cation dominates with the colors of purple, red and orange. As pH values increase, kinetics and thermodynamic struggle happens between hydration reaction of flavylium cation and the deprotonation of acidic hydroxyl group [75].

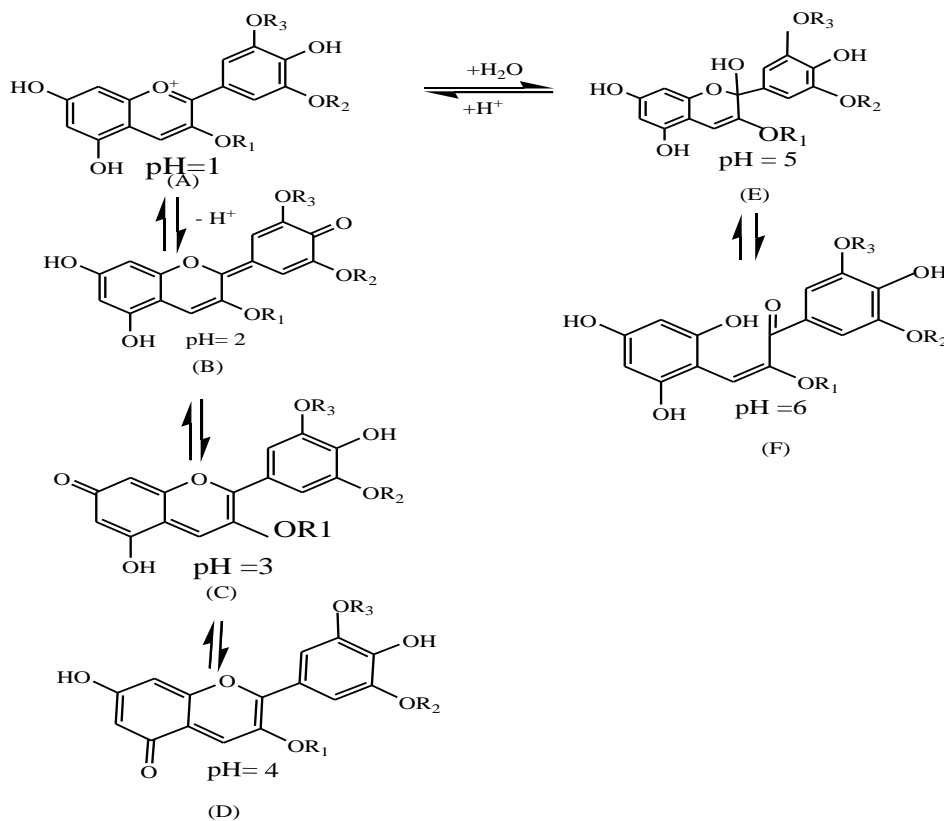


Figure 8: Chemical form of anthocyanin at different pH level in the solution [75].

2.2.3.7 *Persicaria lapathifolia*

Persicaria lapathifolia is one of the species of *Polygonaceae* family that can appear, flowers and ripens from June to October. Other common names for the plant include pale smartweed, curlytop knotweed and willow weed. It grows in marshy places, ditches, canals, small rivers, flood drainage, etc [76]. It is widely available in different countries such as; North America, Europe, South Africa, Ethiopia,... etc [77,78]. Different studies have been made based on different parts of this plant (flowers, leaves, seeds, roots and stems) for different purposes like antibacterial activities, food colorants, beverage, cosmetics,...etc have reported that anthocyanins, flavonols, chalcones, ... etc. are dominantly available phytochemicals in it [79-81]. But its application has not been yet attempted for DSSC preparation although it has appropriately relevant pigments for DSSC fabrication. So that this study has come up with this plant's components (roots and flowers) for DSSC fabrication.

2.2.3.8. Plant material extraction

Plants are complex matrices, producing a range of secondary metabolites with different functional groups and polarities that have various applications in medicinal, food colorant and dye sensitized solar cell fabrication [82]. To get these products we should use different organic solvents of varying polarities and selected methods of extraction. Those methods are solvent extraction procedures applied to plant metabolites include maceration, ultrasound- assisted solvent extraction, percolation, Soxhlet extraction, pressurized solvent extraction, extraction under reflux, steam distillation, and acid-base extraction [83]. However, among these listed extraction methods only maceration was deliberately selected in this thesis to be used.

2.2.3.9. Optical absorption and energy band gap

Sensitizers necessarily have wide and passionate absorption spectrum in the solar spectrum of UV-Vis region, 200-800nm, so as to absorb sufficient photons [84]. Titanium dioxide as a semiconductor has a wide band gap of 3.0 eV (the rutile phase) and 3.2 eV (the anatase phase) can only a small fraction of the sun's energy (mainly ultraviolet region) be used in solar energy conversion. To scale up the light absorption capacity of TiO_2 in the visible region in order to convert solar energy into electrical energy it is usually doped or sensitized with dye molecules [85]. It is noticeable that a photon with energy $h\nu \geq E_g$ can be absorbed in a semiconductor, where E_g is the band gap of the semiconductor. A photon that has less energy than E_g is unable to excite an electron from the valence band to the conduction band. Hence in a pure

semiconductor, there is negligible absorption of photons with $h\nu < E_g$. This confirms that why some materials are transparent in certain wavelength ranges [86]. If a flux or packet of photons with $h\nu > E_g$ falls on a semiconductor, there shall be some appreciable amount of absorption determined by the properties of the material. In this phenomena the ratio of transmitted to incident light intensity depends on the photon wave length and the thickness of the sample. Therefore, the intensity of light transmitted through the sample of thickness, t , is given by;

$$I = I_0 e^{-\alpha t} \text{-----6}$$

Where, α is the absorption coefficient, I_0 is the incident photon beam intensity and I is the transmitted intensity.

The optical absorption coefficient (α) can be calculated from transmittance by using the relation,

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \text{-----7}$$

or

$$\alpha = \frac{2.303xA}{t} \text{-----8}$$

Where, T is the transmittance and t , is the thickness of the sample [87].

Near the absorption edge, the absorption coefficient is expressed with **Tauc** equation;

$$\alpha h\nu = A(h\nu - E_g)^m \text{-----9}$$

Where, A is the optical constant that depends on the properties of material, related to the effective mass of the electrons and hole, α is the absorption coefficient, E_g is the optical band gap and m value is $\frac{1}{2}$ for direct transitions and 2 for indirect transitions [88].

$$E_g = \frac{1240.8 \text{ eV.nm}}{\lambda} \text{----- 10}$$

Where, λ is absorption wave length

Extrapolating the linear part of the curves to the x- axis from the plot of equation 9, $(\alpha h\nu)^{1/m}$ vs. $h\nu$, yields the absorption energies, which corresponds to the favorable band-edge positions for strong optical absorption [89]. Generally after light absorption is taken place at materials there are two types of optical transitions, direct and indirect, happen. Both of them can happen due to the interaction of electromagnetic wave with the electron at the valence band and causes to

raise the electron across the fundamental gap to conduction band. But, indirect transition associated with simultaneous interaction with vibration of atoms or molecules in the gap because the top of valence band maxima with bottom of conduction band minima are not straightly aligned. Consequently, the wave vector of the electron can be changed in the optical propagation in indirect transition. While having been the reverse is true for direct transition, both momentum and energy are conserved in it [90].

2.2.4. Electrochemical properties

2.2.4.1 Cyclic voltammetry

Cyclic voltammetry is a method for investigating the electrochemical behavior of a system and it utilizes three electrodes /working, counter and reference/ electrochemical cell. It is the most widely used technique for acquiring qualitative information about electrochemical reactions as well as offers a rapid location of redox potentials of the electro-active species [91]. As the potential is swept back and forth precede the formal potential, E° , of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte /electro active species/ in solution, confirms cyclic voltammetry to be used in an analytical determination of concentration [92]. The current measured during this process is frequently normalized to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. Through all the processes the most important points ought to be considered in cyclic voltammetry are two cathodic peaks and two anodic peaks [93].

The sensitizing dye can also be electrochemically characterized by cyclic voltammetry and the redox potentials, HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and band gap energies (E_g) of dye molecule can be determined [94].

$$E_{\text{HOMO}} = -(E_{\text{OX}} + E_{\text{REF}}) \text{ eV} \text{ ----- 11}$$

$$E_{\text{LUMO}} = -(E_{\text{RED}} + E_{\text{REF}}) \text{ eV} \text{ ----- 12}$$

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_g \text{ ----- 13}$$

$$E_{1/2} = \frac{(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \text{ ----- 14}$$

Where, E_{REF} , is reference potential.

2.2.4.2. Electrochemical processes

The electron transfer at the interface between the electrode and electrolyte is crucial to an electrode reaction. The electro-active species are diffused or derived to the electrode surface from bulk to give toward or take up electron and result the current to be observed. The transfer of electrons to or from the substrate is an activated process [95]. Actually there are three electrochemical processes;

a/ Reversible process; both forms of redox couple (O for oxidized form and R for reduced form) are stable in the time scale of measurement. In this process the rate of reaction is fast enough to maintain equal concentration of the oxidized and reduced species at the surface of electrode [96].

b/ Irreversible process; For an irreversible process, only forward oxidation or reduction peak is observed but at times with a weak reverse peak. This process is usually due to slow electron exchange or slow chemical reactions at the electrode surface. In an irreversible electrode process, the mass transfer step is very fast as compared to the charge transfer step [97].

c/ Quasi-reversible process; Quasi-reversible process is intermediate between reversible and irreversible systems. The current due to quasi-reversible processes is controlled by both mass transport and charge transfer kinetics [98].

2.2.4.3 Electrodes

An electrode is a material that conducts an electricity by making electrical contact with a nonmetallic part of a circuit (e.g. an electrolyte). There are three types of electrodes that may be incorporated in cyclic voltammetry [99].

a/ Working electrode; The working electrode is apart in an electrochemical system on which the reaction of interest occurs. Eg. Glassy carbon, graphite,...

b/ reference electrode; A reference electrode is an electrode which has a stable and well-known standard potential. eg. Ag/AgCl, SCE, NHE, ... etc.

c/ counter electrode; is along with the working electrode, provides circuit to complete which current is either applied or measured. Eg, platinum wire, ... etc.

2.2.4.4 Pencil graphite electrode.

The graphite pencil electrode (GPE) has been used as working electrode by replacing expensive glassy carbon in modern electro-analytical field due to its high electrochemical reactivity, good mechanical rigidity, low cost technology and simple, renewal, disposability and low background current [100,101].

Limitation of DSSC

- ❖ The liquid electrolyte may suffer from leakage and affected by oxygen, pH, temperature that may cause its degradation and it needs to be substituted with solid electrolyte if possible.
- ❖ The temperature resistant glass as well as sealants should be used.
- ❖ Its efficiency has been still low and for this reason the optimization work should be consistently continuous till the problem is solved.

CHAPTER -THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Apparatus and chemicals

Transparent Conductive Glass Plates (FTO Electrodes, TECHINSTRO, India.), adhesive tape, china, glass rod, Graphite of pencil(NATARAJ), drawing Pencil, China), pH meter(ATC,Scinet group,353), volumetric flask, stainless steel knife, Pipette, beakers, test tube, cuvette(1 cm), digital analytical balance(KERN,ABJ220-4NM), Sonicator (Elmasonic, S10), reagent bottle, measuring cylinder, magnetic stirrer, thermometer, conical flasks, pestle and mortar, Binder clips, tissue paper, aluminum foil or parafilm, fluorescent lump(9 W).

The important chemicals used were; Potassium iodide/KI, INDENTA, chemical, INDIA, Pvt, analytical reagent/,Iodine/I₂, INDENTA, chemical, INDIA, Pvt, analytical reagent /, TiO₂(powder, Sisco Research Lab. Pvt. Ltd, Maharashtra; INDIA), CH₃COONa.3H₂O(Alpha chemical Laboratory Reagent, INDIA), ethanol(96%, HAYMAN Ltd), HCl(37%), Standard pH=6.4 and 4.0 buffer solutions(Blulux, Laboratory(P) Ragent, Ltd), n-hexane(99%, LOBA chemie Laboratory reagents), chloroform(99%, Blulux® Laboratory(P), Ltd, analytical reagent), ethyl acetate (99%, HAYMAN Ltd), Acetone(99.8%, Blulux Laboratory(P), Ltd, analytical reagent), 0.1M NaOH(Blulux Laboratory(P), Ltd, analytical reagent), 0.1 M HNO₃(69-72%, Blulux Laboratory(P), Ltd, analytical reagent), acetonitrile(99.5%, LOBA chemie Laboratory reagents, Mumbai, India), 0.1 M KNO₃(NICE, Laboratory Reagent), 0.1M KCl(Blulux Laboratory(P), Ltd, analytical reagent), Mg slice(Riedel-de Haen), H₂SO₄(98%, Blulux Laboratory(P), Ltd, analytical reagent), Triton x-100(bought from Sisco Reaserch Laboratories Pvt. Ltd, India), FeCl₃(Blulux Laboratory(P), Ltd, analytical reagent) , NH₃(25%, LOBA chemie Laboratory reagents) ,glacialceticacid(99.5%, Blulux Laboratory(P), Ltd, analytical reagent),

Instruments

The instruments used in this work were; electrical oven (N50C, GENLAB,WIDNES, ENGLAND); hot plate (BIBBY,STERILING,LTD,STONE,STAFFORDSHIRE,ST15 0SA,UK); UV-vis spectrophotometer(6705 UV-Vis, JENWAY); Cyclic Voltammetry analyzer (CV, Basi Epsilon-EC-Ver.1.60.70-XP); Extech- Multiviews digital multimeter(MV 120).

3.2 Methods

3.2.1 Collection and preparations of the study plant

The samples of *Persicaria lapathifolia* flowers and roots were collected from Jimma University main campus and Jimma town. Both samples were thoroughly washed with water to remove the adhering particles and dust from the surface. After that both samples were dried in airy room physical and analytical chemistry research laboratory for two weeks and crushed with mortar and pestle to become fine texture [102]. The prepared dry samples were soaked in acidic ethyl alcohol and after 24 hrs they were filtered. These each extracts were taken to rotary evaporator to remove the solvent and the thick mess dyes were obtained. The resulted dyes were used as sensitizer and the left extra dyes were kept in amber bottle in the dark place for another next demonstration of DSSC preparation. The extracted dyes solutions were ensured out of strike of light incidents for degradation of dyes might be caused [03].

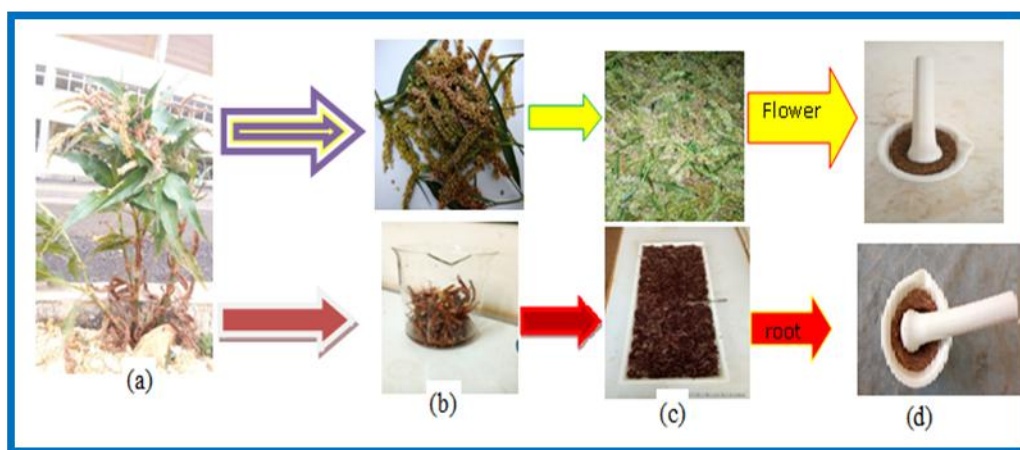


Figure 9: samples of *Persicaria lapathifolia* flowers and roots; (a) for *P. l*, (b) for samples were being washed, (c) for samples were being dried and (d) for samples were being ground.

3.2.2 Extraction and analysis of natural dyes from study plant

3.2.2.1 Maceration

Before bulk soaking was taken place both root and flower samples had checked with various solvents to see solvent effect in extraction in order to lead unbiased decision for appropriate solvent selection. For this reason, the following solvents were used; ethanol, acetonitrile, water and their mixture with concentrated HCl and glacial acetic acids. After observing the absorbance of the both samples extracts with above mentioned solvents the high absorbance measured solvents were selected for bulk soaking. In such ways the root had better absorption

spectra in ethanol with concentrated HCl and flower had better absorption spectra in ethanol with glacial acetic acid. As a result, inferring this premise 20 g of each of sample was individually taken in to separate 500 mL conical flasks. 200 mL of 96% ethanol: 37% of HCl in 99:1 ratio was added in to conical flask with root sample and another 200 mL the same ethanol to glacial acetic acid (85:15) was added to conical flask with flower sample for extricable at room temperature in a darker room. After 24 hrs the solid residues found in the solution was filtered out with filter paper (whatman filter paper 541-110 mmØ) to separate supernatant as natural dye solution from solid gangues waste and the filtrate were taken to the rotary evaporator to remove solvent from dye solution, to make concentrated thick extract. The concentrated dyes were kept for sensitization in appropriate container in the dark at room temperature in amber bottle [104].

3.2.2.2 Phytochemicals screening

The collected plant extracts were subjected to qualitative phytochemicals analysis for identification of various classes of active chemical constituents based on previously had investigated standard methods.

The screening tests were targeted to see flavonoids, polyphenols, anthocyanins, coumarins, anthraquinines, quinines and glycosides. Thus, the phyto-chemical screenings of both flower and roots of *Persicaria lapathifolia* were accomplished with some important chemical as Table 4.

3.2.2.3 Optical properties

The optical absorption of both root and flower extracts as well as their conjugation with TiO₂ for dye loading investigation were measured by UV-Vis spectrophotometer for determination of optical properties. 1 mL of concentrated root and flower of *Persicaria lapathifolia* extract were taken in 25 mL volumetric flasks in separate and diluted with their respective solvents. Then after 1ml of the sample from the test solution was taken and diluted to 10 mL by using buffer of pH=4.5(sodium acetate/ acetic acid). The samples were put into cuvettes of 1cm path length for absorbance reading at different wavelength ranges from 400-800 nm having been used buffer solution as blank [109] and the data were recorded for absorbance vs wavelength plot. Secondly the sintered TiO₂ paste was added to both dye solutions in separate beakers over night to get dye molecules became adsorbed on TiO₂ surface. The optical absorbance of the dyed solution data record were taken for both samples at wave length range 400-800 nm to

investigate dye loading effect and also pure TiO₂ absorbance was measured at wave length ranges of 350-800 nm having been dissolved in ethanol and distilled water with the ratio of 4:2 by using as solvent. The optical absorption data were used so as to determine energy band gaps [110].

Table 4: Phytochemical screening test.

Phyto chemicals	Tests in root	Tests in flower	Ref.
flavonoids	a/ 1mL of extract was mixed with 1mL of 2N NaOH.	a/ 2 mL extract was blended with a few drops of 2N NaOH.	[105]
	b/ 5 mL of extract was mixed with 96% ethanol as well as 0.5 g Mg slice and drops of conc.HCl were added.	b/ 1 mL of extract was mixed with NH ₃ solution.	[106]
	c/ 1 mL extract was mixed with a few drops of conc. HCl.	c/ 5 mL of extract was mixed with 0.5 g of Mg slice and drops of conc.H ₂ SO ₄ .	
anthocyanins	a/ 2 mL extract was blended with 2 mL of 2N HCl and NH ₃ solution .	2 mL of extract was blended with conc.H ₂ SO ₄ .	[106]
	b/ 1 mL of extract was mixed 2N NaOH.		
polyphenol	a/ 2 mL extract was blended with 2 drops of 2% FeCl ₃ .	a/ 2 mL of extract was mixed with a few drops of 10% FeCl ₃	[107]
	b/ 1 mL extract was mixed with 10% NaOH	b/ 2 mL of extract was mixed with 2 mL 2N HCl.	
coumarins	1 mL extract was blended with 1 mL 10% NaOH.	1 mL of extract was mixed with 1 mL 10% NaOH.	[108]
glycoside	1 mL extract was blended with 2 mL of Chloroform and 1 mL of ammonia solution.	1 mL of extract was blended with 2 mL of chloroform and 1 mL of ammonia solution.	[108]
quinine	1 mL extract was mixed with a few drops of conc.H ₂ SO ₄ .	2 mL of extract was mixed with a few drops of conc.H ₂ SO ₄ .	[108]
Anthraquinine s	1 mL of extract was mixed with.	1 mL of extract was blended with NH ₃ .	[108]

3.2.2.4 Electrochemical analysis of prepared dyes

The electrochemical potential of extracted natural dyes was analyzed by cyclic voltammetry [111] while using pencil graphite as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. Having been three electrodes were connected with potentiostat it was scanned at rate of 50 mV/s throughout the potential windows from -0.3 to 0.7 V by using 0.1 M KNO₃ as supporting electrolyte [112]. Pencil/4B/ graphite lead with (a diameter of 1.5 mm and resistance of 7 Ω) was drawn from its holder, wrapped with parafilm and inserted in to micro-pipette glass having been made electrical contact by connecting copper wire along back side. Only the tip is left and the side of exposed part was covered with parafilm to prevent side way solution contact in order to make safe for active area presumption at tip of electrode [113].

1 mL of both dyes solution were taken after being diluted with their respective solvents in ratio of 1:10 and again 1 mL of the diluted solutions were separately mixed with 10 mL sodiumacetate-acetic acid buffer (pH=4.5/ 0.1 MKNO₃). Finally, the cyclic voltammetry analysis was conducted and the buffer/ electrolyte used as blank solution, reference. The system was run on a PC using Basi Epsilon-EC-Ver.1.60.70-XP Voltammetry and before each subsequent analysis; the working electrode was being polished, followed by cleaning in an ultrasonic bath for 5 min. with distilled water; thoroughly rinsed with ethanol and acetonitrile [114].

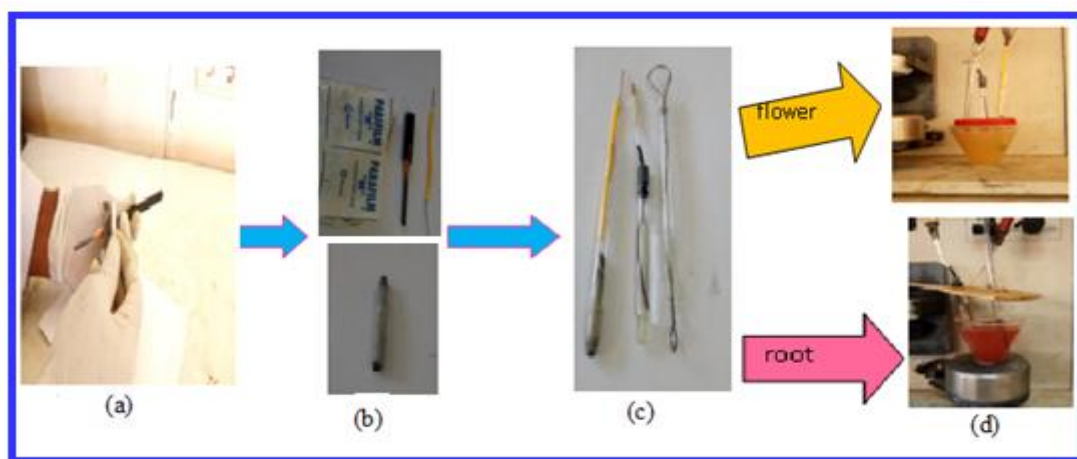


Figure 10: preparation of working electrode from pencil graphite and cyclic voltammetry; (a) for graphite electrode was being unsheathed, (b) for graphite electrode was being wrapped with parafilm and connected with copper wire, (c) for working, reference and counter electrodes; and (d) for cyclic voltammetry set up.

3.2.3 Preparation and assembly of DSSC

3.2.3.1 Preparation of the FTO glass

2.5 cm × 2.5 cm FTO glasses with sheet resistance of 26 Ω/cm^2 (were bought from TECHINSTRO, India) were cleaned in a detergent solution by using an ultrasonic bath for 30 min, rinsed with water, ethanol and then dried in an oven at 60°C for 30 min [115].

3.2.3.2 Preparation of TiO₂ electrode (photo anode)

The TiO₂ film was prepared by mixing 6 gm of commercial TiO₂ powder bought from Sisco Reaserch Laboratories Pvt. Ltd, India, 9 mL of nitric acid solution (0.001M) with successive increment of 1 mL in mortar and pestle. To have white free paste 8 mL of distilled water was added with 1 mL increment while grinding was continuous. Finally, 0.05 mL of transparent surfactant (Triton x-100, bought from Sisco Reaserch Laboratories Pvt. Ltd, India) was added with 1 mL of distilled water to ensure coating uniformity and adhesion to the transparent conducting glass electrode [116]. The mixture was nicely homogenized by using an ultrasonic bath for 30 minutes and stirred for 48 hrs and the resulting paste was carefully spread over an FTO conductive glass plate having a resistance of 27 Ω/cm^2 , transmittance of 79% and the active area for DSSC was made to be 1 cm² (1.0 cm × 1.0 cm) by using adhesive tape. Successively the TiO₂ paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer, to control paste thickness and helps to let conductive off site for electrical contact, by Doctors'-blade technique. After 20 minute the TiO₂ thin film was sintered at 450 °C for 1h to increase compactness of the thin film and confirmed by heat treatment, in order to increase the internal void of film organization and enhance its absorption performance. Then after the sintered TiO₂ thin film was immersed in natural dyes prepared for 24 hrs so as to the natural dye molecules to be adsorbed on the surface of TiO₂ film semiconductor. The anhydrous alcohol was used to remove any natural dye that had not been adsorbed on the surface of TiO₂ thin film. After all the steps, photo-electrode was completed and ready for testing [117].

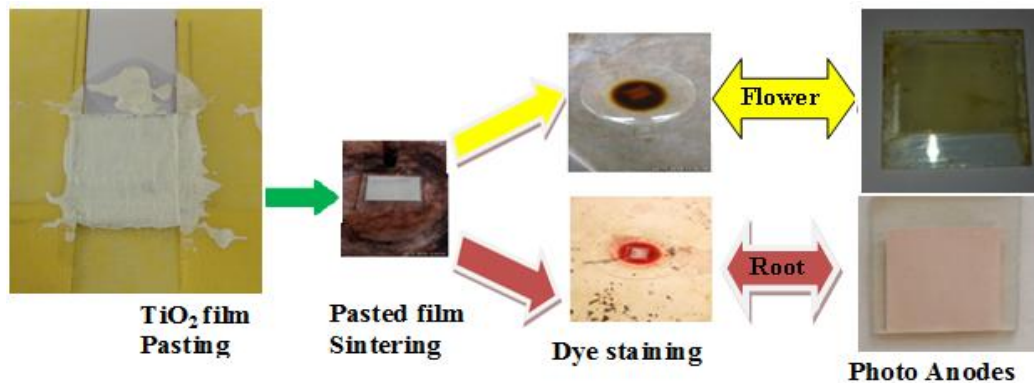


Figure 11: preparation of photo anodes

3.2.3.3 Preparation of counter electrode (cathode)

To make the carbon counter electrode, the FTO glass was managed to be wiped with ethanol and the graphite-coated slide, the conductive side of the glass plate was coated with carbon by gently sweeping the surface with a graphite stick (2B pencil) [118]. Next, the carbon-coated glass plate was coated with black by holding the carbon-coated side of the glass plate above a candle flame and the surface was checked to ensure that there had no space that non carbon covered site. Then, the carbon coated glass plate was heated on a hot plate at 60°C for 16 minutes and allowed to cool at room temperature before with draw out from oven [119].

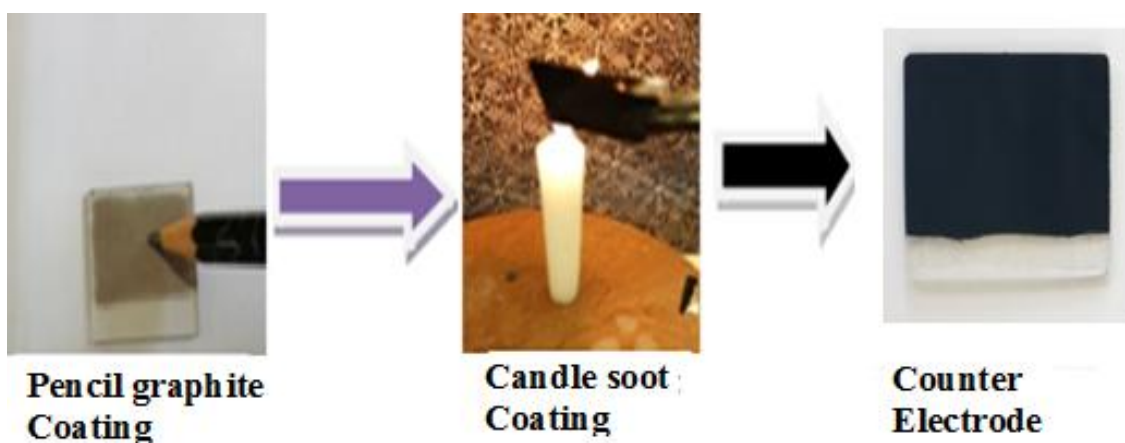


Figure 12 preparation of counter electrode

3.2.3.4 Preparation of electrolyte

The liquid electrolyte solution was prepared by transferring 50 mL of acetonitrile into 200 mL beaker. Then after, 8.3 gm of potassium iodide was added into the beaker that containing acetonitrile and stirred well with magnetic stirrer until dissolved. Following that the mixture was transferred to 100 mL volumetric flask, 1.27 gm of iodine (I_2) was added in to the volumetric flask and the mixture was made to 100 mL with acetonitrile [120].

3.2.3.5 DSSC Assembling

The cells were assembled by both the graphite-coated counter electrode and the dye stained titanium dioxide coated working electrode sides were made to face toward each other. The two electrodes were placed one on top of other with a slight offset to guarantee that all of the stained titanium dioxide film was covered by the counter electrode and a space left for connecting the multi-meter crocodile clips for electrical parameters measurement. Next two binder clips were used on opposite edges to gently hold the slides together. A few drops of the iodide/iodine electrolyte solution were placed at the edges of the plates to percolate into the cell by capillary action. Afterward, the two binder clips were alternately opened and closed so as to promote the uniform dispersion of the iodide/iodine electrolyte between the slides. Finally, the alligator clips were attached to the overhanging edges to be connected to the multi-meter with respective polarity, negative and positive terminals, stained titanium dioxide (working electrode) and graphite stained (counter electrode) slides, respectively [121].

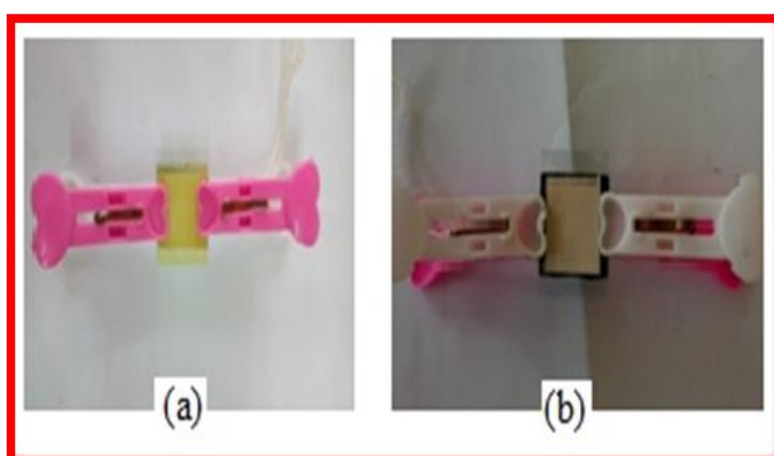


Figure 13: Assembled DSSC of flower (a) and root (b)

3.2.3.6 Characterization of prepared DSSC

The performance of each prepared DSSC was characterized based on the parameters such as short circuit current (I_{sc}), open circuit voltage (V_{oc}), optimum voltage (V_m), optimum current (I_m), fill factor (FF) and efficiency (η) and an incident Photon to Current conversion Efficiency (IPCE) by using Extech Multimeter [122, 123].

Light Source

Two light sources were used for illumination of the cells in this thesis. First, 9 W fluorescent light bulb at 4.5 cm height from the surface of the anode was used by adopting a similar setup (35 W light bulb at 15 cm), a light intensity of $40 \mu\text{W}/\text{cm}^2$ was used by Liu et al [124, 125]. If the beam of light intensity is fallen onto a circular area, then area is proportional to the square of the distance to the lamp. Hence, if the distance is doubled the light intensity per surface area unit is reduced by a factor of quadruple. From this premises the light intensity was estimated to be $114.25 \mu\text{W}/\text{cm}^2$ at the electrode;

$$\frac{35\text{W}}{F(15\text{cm})^2} = 40\mu\text{W}/\text{cm}^2 \text{ ----- 15}$$

$$F = \frac{35\text{W} \times \text{cm}^2}{40\mu\text{W} \times (15\text{cm})^2} = 3890 \text{ ----- 16}$$

Therefore,

$$\frac{9\text{W}}{F(4.5\text{cm})^2} = 114.3\mu\text{W}/\text{cm}^2 \text{ ----- 17}$$



Figure 14: Illuminating light source from 9W fluorescent lamp(a), circuit and Multimeter (b)

The second light used was sun light at noon. By using Extech multimeter the voltage and current readings were taken at mid day assuming that the sun would give $100\text{mW}/\text{cm}^2$ as incident power at the global air mass of 1.5 [126,127]. The data were taken by designing

electrical circuit on the wood board with various electronic resistors in series connection as load to estimate I-V curve. The voltage readings were taken by connecting multimeter in parallel with DSSC and circuit board. The maximum resistance for V_{oc} where current reading became zero and minimum resistance for I_{sc} where voltage reading became zero were determined. Beyond this voltage readings with each resistor were recorded and the currents were calculated from the measured voltage with respective resistance based on Ohm's law/ $V = I R$. Having been taken these data the prepared DSSC were characterized by plotting I-V, P-V and IPCE curves [128].

CHAPTER-FOUR

4.0 RESULTS AND DISCUSSION

4.1 Extracted dye

From soaked samples the filtrates as natural dye have red color for root extract and yellow color for flower extract were obtained. After all solvent contents had been evaporated 8.84 gm for root and 9.3 gm for flower crude dye were collected.

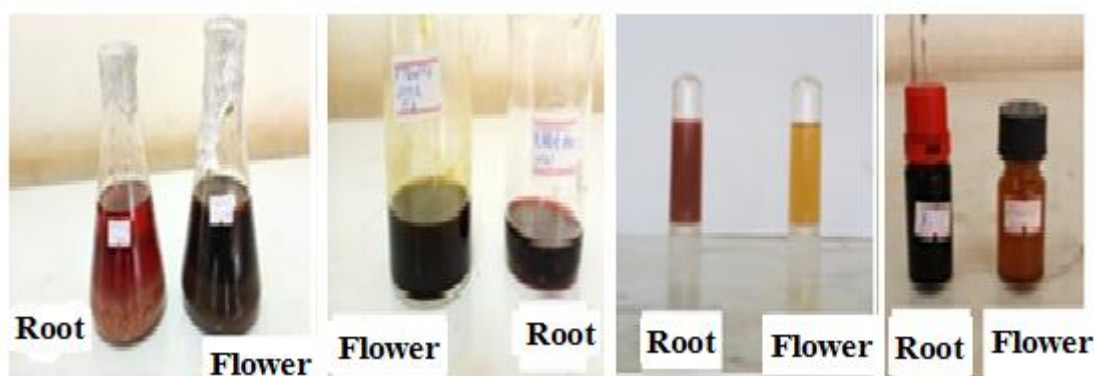


Figure 15: extracted dyes of *Persicaria lapathifolia* roots and flowers.

4.2. Optical Characterization of Dyes Solution

The extracted *Persicaria lapathifolia* root and flower dyes absorption spectra were recorded by using UV-Vis spectrophotometer in the wave length range of 400-800 nm and the result is indicated in the figure 16. The appearance of absorption spectra peaks of root extract at wavelength of 462 and 654 nm; spectra for flower extract at wave length of 535, 606 and 666 nm indicate that both root and flower dyes may be used as an anticipating photo-sensitizer of DSSC due to its good absorbance in the visible spectrum region [129]. The UV-Vis data indicates that in both root and flower extracts there are anthocyanin such as Peonidin-3-*O*-acetylglucoside-4-vinylcatechol and Delphinidin-3-*O*-acetylglucoside-4-vinylphenol(462nm) [130], cyaniding (535nm) [131]. Other peaks at wave length of 654nm for root extract as well as 606 and 666 for flower extract were due to the pigment of chlorophylls as considered to be residue and anthocyanins [132-134]. The same anthocyanin/pigments/ may have different possible colors at different wave length depending on solvents polarity, pH variations in the solution and co-pigmentation through intermolecular or intramolecular bonding [135,136]. In similar way of spectrophotometric determination of dyes mixed with sintered TiO₂ was carried out to see the effect of dye adsorption on TiO₂ in the absorption spectrum.

The enhancement of absorbance to hyper chromic shift and appearance of spectra red shift for root dye with TiO₂ are 466, 665 nm and for flower dye with TiO₂ are 540, 614 and 670 nm indicate that the anchoring and chemical interaction of complex formation of the dye molecules to the TiO₂ photo anode [137]. As a result, the efficient charge transfer and high quantum yield facilitated [138].

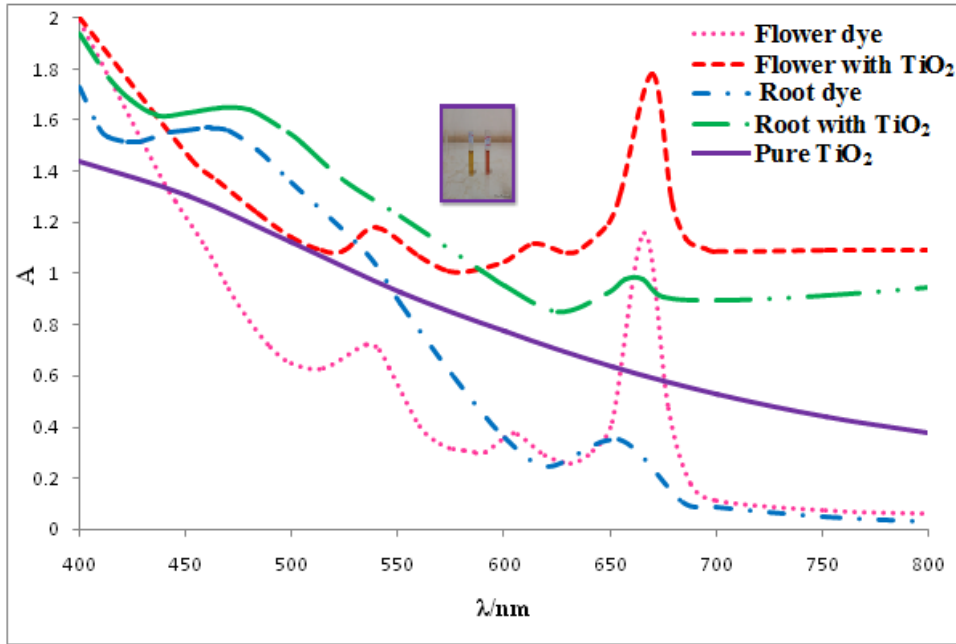


Figure 16: Absorption spectra of flower dye, flower dye with TiO₂, root dye, root dye with TiO₂ and pure TiO₂.

4.3. Band gap analysis

The optical absorptions of *Perssicularia lapathifolia* flower and roots extract as well as pure TiO₂ were measured in the wave length range of 400-800 nm. From the recorded results the absorption spectrum analysis and absorption coefficient calculation (equ.8) as a function of photon, band gap energy (equ.10) were carried out.

The band gap energy, E_g, near the absorption edge can be further determined using the following expression: $\alpha h\nu = A(h\nu - E_g)^2$.

As a result, the plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ were performed and the optical band gaps energy were obtained from the plot by extrapolating from the straight line part /slope/ curve to the x-axis/ $h\nu$, at $\alpha h\nu = 0$, as shown in figure 17 [139,140]. These graphs illustrate the energy band gap shift to lower level after sensitization than pure dyes and TiO₂ do show.

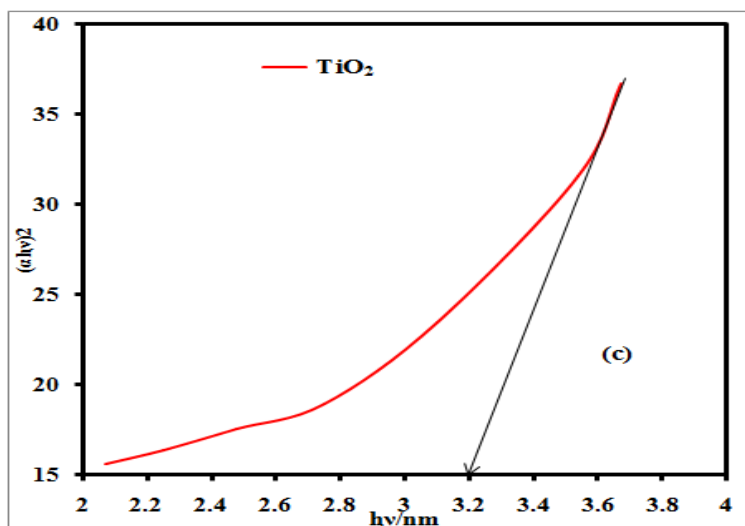
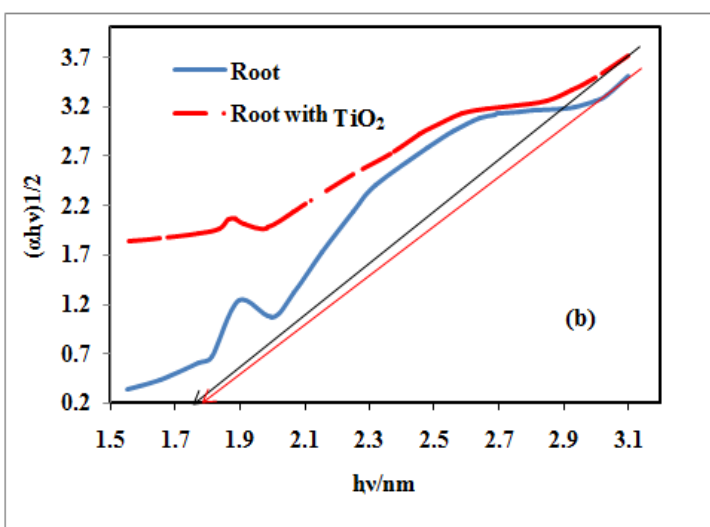
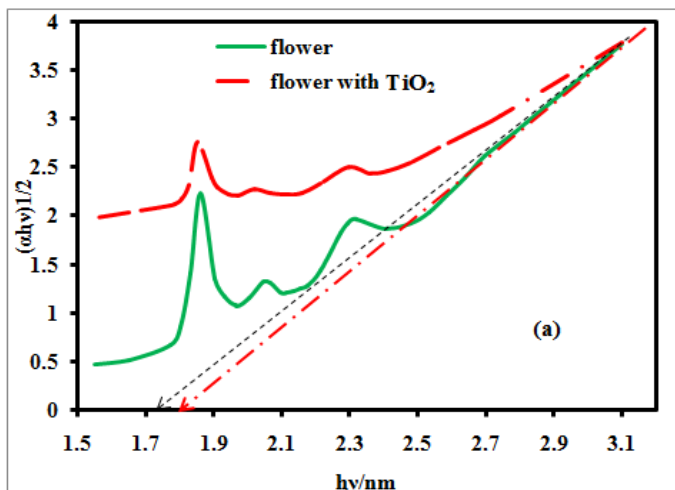


Figure 17: Optical band gaps energy of (a) flower dye; flower dye with TiO₂, (b) root dye; root dye with TiO₂ and (c) Pure TiO₂.

In non crystalline natured dye and dye adsorbed film optical transitions were assumed to be described to a first approximation by non-direct transitions as the processes governed by hopping mechanism by diffusion with no conservation of electronic momentum, for allowed indirect transitions $n = 2$ whereas the crystalline for pure TiO_2 the optical transition was stipulated as direct transition with conservation of momentum, no change in wave factor, for allowed direct transition $n = \frac{1}{2}$ [141]. Based on these presumptions all the relevant data concerning optical absorbance and band gap energy estimation were listed in Table 5.

Table 5: maximum absorption wave length and band gaps for pure dye extract and their adsorption on TiO_2 surface.

	$\lambda_{\text{max}}, \text{nm}$	$\lambda_{\text{onset}}, \text{nm}$	$E_{g(\lambda_{\text{max}})}, \text{eV}$	Band gap energy, $E^{\text{onset}}, \text{eV}$
Root	654	693	1.9	1.79
Flower	666	689	1.86	1.801
Pure TiO_2	376	387.8	3.3	3.2
Root + TiO_2	665	700	1.866	1.77
Flower + TiO_2	670	703	1.852	1.77

It is clearly evident that after dye sensitization the optical absorptions of the TiO_2 film and dyes were improved. As result of this the band gaps of sensitized films were decreased in comparison to the pure TiO_2 film and dyes, which makes the flower and roots of *Persicaria laphatifolia* dye coated thin film suitable for the solar cell applications. The optical band gap decreasing trend of the film upon dye sensitization indicates the easiness for charge transfer/electron jump up/ was made to be facilitated.

4.4 Phytochemical screening

The main aim of phytochemical screening is to identify the natural chemical compounds present in a given plant extract which may be responsible for the intended light absorption for sensitization of TiO_2 by using appropriate chemicals. Hence, Photo-chemically active and electrochemically responsible compounds were identified from the extract of *Persicarial laphatifolia* roots and flowers by phytochemicals screening test protocol. Among the screened compounds/components; flavonoids, polyphenols, anthocyanins, quinones, anthraquinones, coumarins and glycosides were the main and important items for DSSC fabrication [142,143].

The phytochemical tests were done according to Table 4 above and the following observations were recorded.

Table 6: The results of Phytochemical screening for roots and flower extracts

Phytochemical tests	Observation		Results and indication	Ref.
	Root	Flower		
flavonoids	Yellow,pink,red	Yellow	Flovonids exist in both root and flower	[144]
anthocyanins	Pinkish red, bluish green	Orange yellow	Anthocyanins exist in both root and flower	[145]
poly phenol	Blue black	Green blue/yellow	Polyphenols exist in both root and flowe	[145]
coumarin	Yellow	Yellow	Coumarins exists in both root and flower	[146],
glycosides	Pink	Yellow	Glycosides exist in both root and flower	[147]
quinone	Red	Yellow*	Quinines exist in root, but doesn't in flower. Because no red.	[147]
anthraquinones	Pink	Orange or yellow*	Anthraxquinones exist in root but doesn't in flower. Because no pink	[148]

(*) indicates for another unexpected compounds that may be found in *Persiccaria lapathifolia* flowers extract.

As data shown in Table 6 above from root dye flavonoids, anthocyanin, polyphenols, coumarin, glycosides, quinine and anthraquinones were phytochemically screened where as from flower dye flavonoids, anthocyanin, polyphenols, coumarin and glycosides were phytochemically determined. However, quinone and anthraquinone were not found from flower dye. Although quinine and anthraquinones were not obtained from flower extract, other unexpected compounds are available as yellow and orange colors were observed.

4.5 Cyclic voltammetry

Cyclic voltammetry analysis was carried out in order to determine oxidation potential by relating with highest occupied molecular orbital (HOMO) and reduction potential by relating with lowest unoccupied molecular orbital (LUMO) of dyes solutions [149]. The oxidation

peaks potential ($E_{pa1}=-0.109$ V & $E_{pa2}=0.469$ V) for root and ($E_{pa1}=-0.125$ V & $E_{pa2}=0.554$ V) for flower of *Persicaria lapathifolia* as natural dyes were obtained with Ag/AgCl in solution as reference electrode [150]. Though no reduction potential peaks of dyes solution were observed, from the relation of band gap energy $/E_g/$ with HOMO level the values were calculated as; $E_{LUMO} = E_{HOMO} - E_g$ and $E_{HOMO} = -e (E_{OX}(\text{onset}) - E_{ref})$ [151-153].

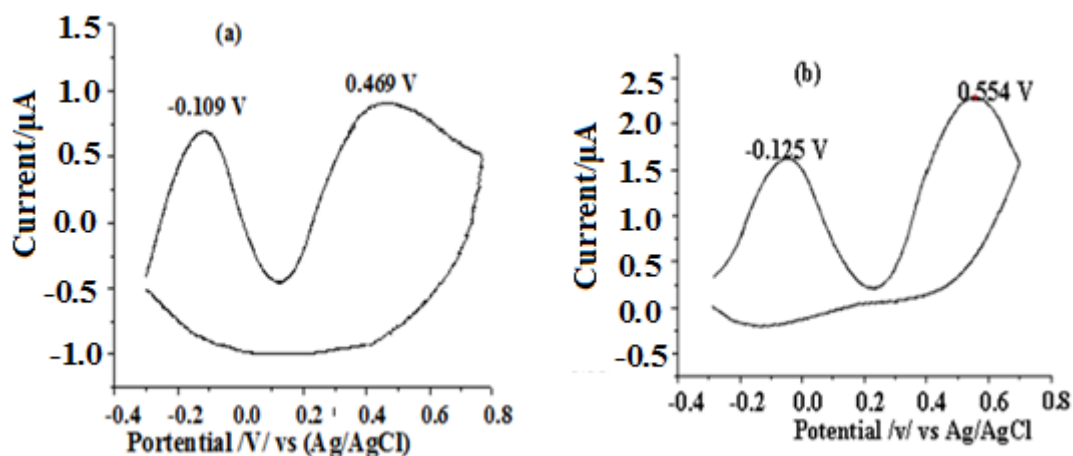


Figure 18: cyclic voltammogram of (a) root dye and (b) flower dye.

The cyclic voltammograms of roots and flowers of *Persicaria lapathifolia* showed that an irreversible electrochemical process of oxidation peaks, while at lower potential the first peak which is attributed due to the oxidation of the hydroxyl groups in the B-ring of anthocyanin and the second peak for oxidation of the hydroxyl groups found at A-ring [154]. In both roots and flowers intense anodic peaks were observed indicate to presume fast electron transfer in oxidation process. This technique illustrates the ability of the compounds to easily donate electrons around the potential of the anodic wave. But, the return cathodic peaks were significantly smaller, confirms that the oxidation products were being rapidly degraded to another chemical entity, that may be reducible at much more negative potentials (possibly associated with the small cathodic peak seen at potentials less than -300 mV) [155]. Both extracts have lower oxidation potential/ lower energy requirement for oxidation of dye/ that sound for higher electrochemical behavior in DSSC fabrication and the first peaks in both cases are responsible for electron injection due to lower peak current [156].

4.6 Energy level calculation

As thermodynamically feasible electron injection from a photo-excited dye molecule at LUMO level into the conduction band of the TiO₂ surface and subsequent regeneration of the dye molecule to its original form can be accessed from the energy level diagram, it has been located with presumably relative positions of the electron exchange energy levels of all of the cell components (semiconductor electrode, dye and redox couple) [157].

Table 7: Calculated energy level and band gap results

Dye extract	LUMO (eV)	HOMO (eV)	E _{ox} , V	E _{red} , V	E _g (λ _{max}), eV
Root	-1.594	0.306	-0.109	-	1.9
Flower	-1.538	0.322	-0.125	-	1.86
I/I ₃	0.28	0.302	-0.105	0.477	-

$$\text{HOMO} = -(E_{\text{ox}} - E_{\text{ref}})e, \text{LUMO} = \text{HOMO} - E_g, E_{\text{Ag/AgCl NaCl saturated solution}}^0 = +0.197 \text{ V [158].}$$

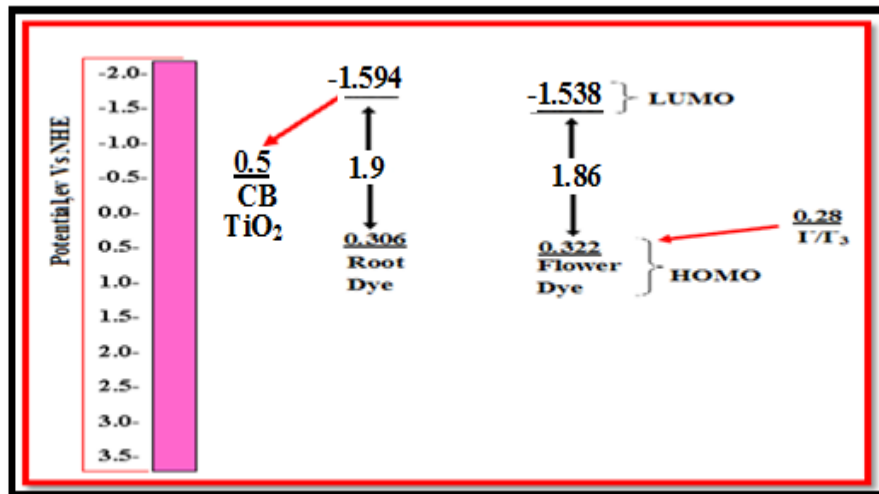


Figure 19: The forecasted energy level diagram for dyes extracted from root and flower of *Persicaria lapathifolia* sensitized solar cell [159].

4.7. I-V curve and photovoltaic performance of DSSCs

The photovoltaic properties of the DSSCs sensitized with the dyes extracted from *Persicaria lapathifolia* roots and flowers with ethyl alcohol as solvent were studied by using Extech multimeter and electrical circuit on wood board made from different resistors as load. The

fluorescent lamp/9W/ and sun irradiance were used as light source and the obtained potentials with respective resistor were used to compute current according to Ohm's law;

$$P = VI \text{-----18}$$

$$I = \frac{V}{R} \text{-----19}$$

$$P = \frac{V^2}{R} \text{-----20}$$

The results were used to characterizing I-V curves as shown in Figure 20. The corresponding photo-electrochemical parameters have been listed in Table 8 [156,161].

The solar cells performances were decided by their overall conversion efficiency (η) and incident photons to conversion efficiency (IPCE). The solar cells outputs were characterized by three known parameters (I_{sc} , V_{oc} and FF). The short-circuit current, I_{sc} , is a current flows freely through measuring circuit that has no load or resistance. Open circuit voltage, V_{oc} , were decided by setting maximum resistance at where no current could flow. Theoretically it is also corresponds to the energy difference between the Fermi level of the semiconductors and the reduction level of the electrolyte redox couple. However, the rate constants/recombination effect/ might limit the V_{oc} so that the theoretically maximal ($V_{oc} = E_{CB, TiO_2} - E_{redox}$) cannot be practically attained but during light illumination as the electron density increases the problem is solved due to the fermi-level shifts as closer as to meets the conduction band [162]. The maximum power was obtained as the area of the rectangle that corresponds to maximum voltage and current that DSSCs produced along load or resistance. From the maximum power point the fill factors (FFs) were calculated, which is quantitative measure of the device's quality defined by the square of the I-V curve [163]. The IPCE is expressed as the ratio of the number of electrons produced and that flow through the external circuit under short circuit current to incident photon at a given wavelength [164,165].

$$IPCE\% = \frac{1240.8 \times J_{sc} (A/cm^2)}{\lambda(nm) \times P_{in} (mW/cm^2)} \times 100 \text{----- 21}$$

J_{sc} , photocurrent density (current per area of DSSC in centimeter square), (λ) wave length and input light intensity (P_{in})

Input power, P_{in} , is the amount of the photons hitting the solar cell surface. For this work, P_{in} from fluorescent lamp was calculated as, 0.1143 mW/cm^2 .

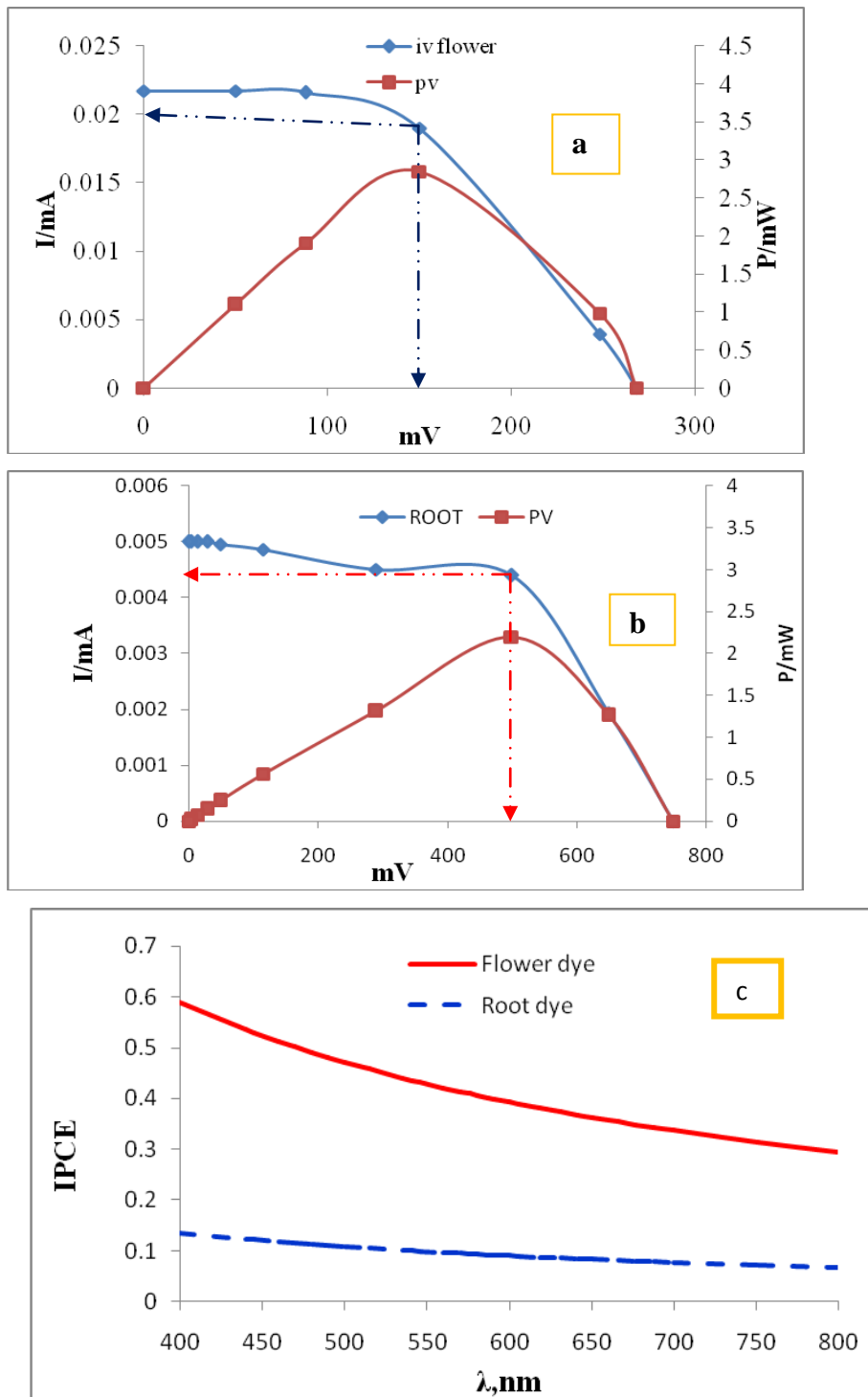


Figure 20: I-V and P-V (a, b) and IPCE (c) curves of a Dye sensitized solar cells under illumination

4.8 Comparing the results of photovoltaic performance of prepared DSSCs with previously fabricated cell in similar research area

There are various works that have been reported regarding DSSCs based on natural dyes as key sensitizers. As they were performed in different laboratories the researchers used different extraction methods, fabrication techniques, light sources, loads...etc. But have the same characterization parameters. Hence, referring these works to present work in order to compare the relevancy and anticipating finding in engaged research area is imperative. So that, the present results and another previously worked DSSCs results are in Table 8.

Table 8: Photovoltaic performance of DSSCs.

DSSCs made from	P_{in} , mW/cm ²	I_{sc} , mA	V_{oc} , mV	P_{max} ,mW /cm ²	FF%	η %	reference
<i>Persicaria lapathifolia</i> Root	0.1143*	0.005	750	0.0022	58.67	1.93	present
<i>Persicaria lapathifolia</i> Flower	0.1143*	0.0217	268	0.00285	49.01	2.49	present
Raspberry	16*	0.60	150	0.03	-	0.19	[166]
Blackberry	16*	0.72	180	0.04	-	0.27	
Grape fruit	16*	0.2	50	0.003	-	0.02	
Spinach leaves	16*	0.08	20	0.0005	-	0.003	
Chlorophylls from <i>Sargassum</i>	0.085*	0.0029	241	0.3003	0.432	1.50	[167]
Rhoeo spathacea	100**	10.9	500	-	27	1.49	[168]
Mangosteen pericarp	100**	2.69	680	-	63	1.17	
Neem leave	100**	15.10	540	-	35	2.81	
<i>Lawsonia inermis</i> seed	100**	2.99	500	-	70	1.47	
Yellow rose	100**	0.74	600	-	57	0.26	
Ivy gourd fruits	100**	0.24	640	-	49	0.08	
Pitaya	100**	0.5	330	-	0.52	0.17	[169]
Rhododendron sp.	100**	0.85	544	-	0.72	0.33	

❖ Indicated by (*) are P_{in} from fluorescent lamp whereas indicated by (**) are P_{in} from solar simulator.

CHAPTE-FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

From the extraction of flowers and roots of *Persicaria lapathifolia* yellow and red colored dyes were resulted respectively. These colors of extracts are responsible for anthocyanins as they were indicated in phytochemicals screening. The pure extracts have shown continuous broader absorption spectra trend in the visible wave length ranges (400-800nm) of the electromagnetic spectrum. But after TiO_2 loading in to dyes the red (bathochromic) and hyperchromic shift to the pure dyes spectra are observed. This indicates that the dye molecules have made bond with TiO_2 surface. From the absorption spectra the optical band gap energies are calculated as for flower 1.86 eV and roots 1.9 eV. The electrochemical oxidation potentials for flowers -0.125 V; 0.554 V and for roots also -0.109 V, 0.469 V were obtained. Consequently, flower extract dye HOMO = 0.322 eV and LUMO= -1.538eV; root extract dye HOMO = 0.306 eV and LUMO = -1.594 eV were determined. In both cases HOMO lies lower than iodide/tri-iodide couple electrolyte redox potential (0.28 eV) and LUMO lie higher than conduction band edge of TiO_2 (-0.5 eV). As a result, these dyes are good candidates for DSSC fabrication. Hence, flower based DSSC with efficiency of 2.49 % and root based DSSC with efficiency of 1.93% were fabricated. Therefore, it is concluded that flower has higher efficiency than root according to this study. However, the distances between conduction band and LUMOs need to be minimized as close as optimum ranges of 0.1-0.3 eV and the distance between HOMOs and electrolyte couple (iodide/triiodide) need also to be increased up to as near as optimum ranges of 0.2-0.3 eV. For these reasons, the further studies should be continued to solve the problems.

5.2. RECOMMENDATIONS

As the FTO glass resistance increase the series resistance increase and the cell efficiency decreases. The FTO glass that has been used in this work is $26 \Omega/\text{cm}^2$ but if it were less than this the efficiency would increase. Therefore, FTO with less resistance, $10\text{-}15 \Omega/\text{cm}^2$ should be used [170].

The higher the film thickness may cause the reduction of electron diffusion length results increasing of electron recombination lowers V_{OC} . Similarly, Short circuit current also decreases starting from a certain thickness with increasing film thickness, because series resistance increases with increasing film thickness. It is caused by the recombination of electrons with I_3^- ions on the TiO_2 surface and hence, lowering the J_{sc} . consequently, the cell performance would decrease. Therefore, the film thickness should be reduced to optimum range, $10\text{-}20 \mu\text{m}$ [171-173].

The reduction potentials of sensitizing dyes were -1.538 eV and -1.594 eV much higher than the recommendable amount $0.1\text{-}0.3 \text{ eV}$ above the conduction band of TiO_2 may causes dark current by increasing recombination and losses of J_{sc} [174]. Therefore, to adjust this mismatch the redox electrolyte should consists of iodides, iodine and additional additives such as tetrabutylammonium (TBA^+), 4-tertbutylpyridine (4-TBP), etc.... These different additives affect the energetic of the semiconductor/dye/electrolyte interface [175]. Changing the nature of the electrolyte can change the position of the conduction band edge of the TiO_2 . The position of the conduction band edge will be at more negative potentials vs. NHE in the presence of negative adsorbed ions and more positive in the presence of positive adsorbed ions. The less positively charged surface with TBA^+ will lead to a negative shift of conduction band edge than in the case of H^+ in comparison. This upward shift of conduction band edge facilitates the as fast as possible the electron injection rash to dominates than recombination occur due to narrowing of the energy difference between conduction band and the dyes reduction potentials [176]. Or else the introduction of electron with drawing groups like CO , COOHetc in to electron accepting part of dyes to shift down LUMO and electron donor groups to the electron donating part of dyes of chromogen to increase HOMO [177].

The used light sources were 9 W of fluorescent lamp; in laboratory non tested binder clips and the direct sun light are not appropriate. Due to the diffusive combined light spectrum and non screened beam the measuring efficiency was not satisfactory. Therefore, the solar simulator should be used for future as solar simulator selects only visible wave length to pass on the

testing cell and solves heat challenges. Appropriate binder clips should be used to safe guard leakage of electrolyte outside of cell that reduces current by making recombination with electrons to the circuit as well as from the circuit [178].

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APPENDIX

Photos

A. Phytochemical results

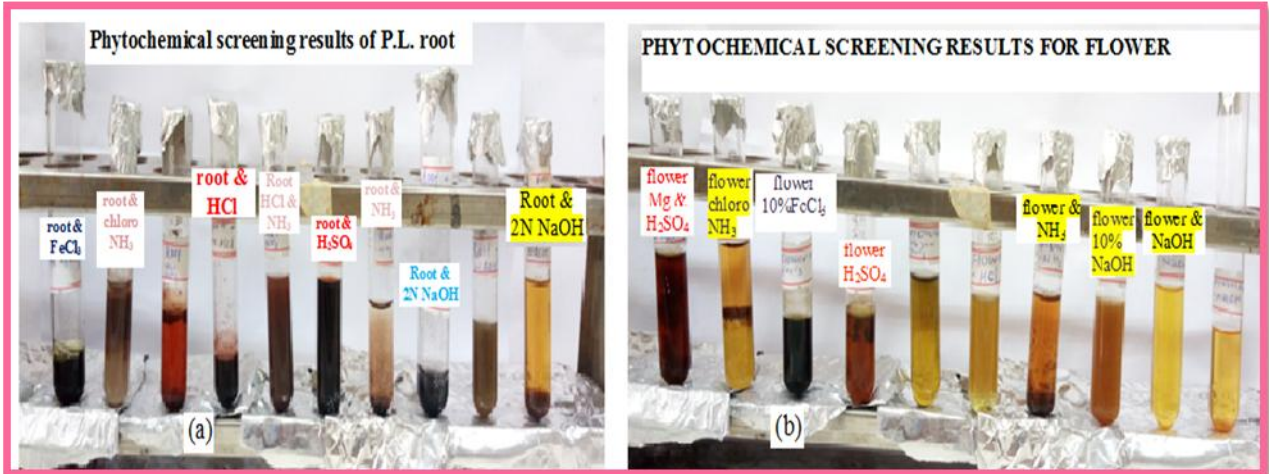


Figure 21: results of phytochemical screening(a) for root and (b) for flower.

B. Photovoltaic results

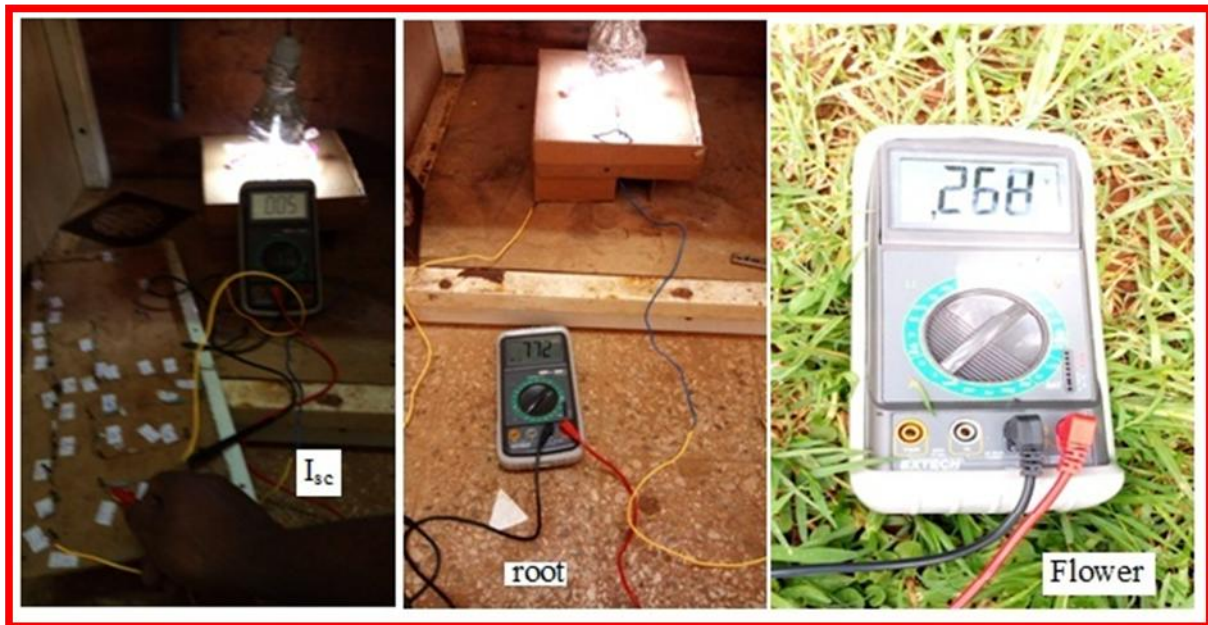


Figure 22: Measuring of voltage to calculate current by using electrical circuit made from resistor and fluorescent lump/9W/.