"Green and sustainable development of photogalvanic cell using Bromocresol green photosensitizing dye for solar energy conversion and storage"

Ravneet Maan
Research Scholar, Dept. of Chemistry, Faculty of Science, Tantia University, Sri Ganganagar (Rajasthan)
Dr. Devender Singh
Research supervisor, Dept. of Chemistry, Faculty of Science, Tantia University, Sri Ganganagar (Rajasthan)

Abstract : Rising concerns about climate change, the health effects of air pollution, energy security and energy access, along with volatile oil prices in recent decades, have led to the need to produce and use alternative, low-carbon technology options such as renewable. The photogalvanic cells as described in the present article are promising energy devices as they provide for a route for simultaneous solar power generation and its storage. The study of photogalvanics of Bromocresol - EDTA - Tween 80 has been studied in alkaline medium at low intense light with aim of searching relatively proper combination of chemicals like photosensitizer, reductant and surfactant for further enhancing the efficiency of PG cell. The best conditions for cell have also been observed for optimal cell performance. The solar conversion efficiency, fill factor, cell performance (as $t_{1/2}$), power at power point, open circuit potential, equilibrium current and charging time at 10.4 mWcm^{-2} has been observed of the order of 0.96%, 0.1448, 100 minutes, 100.13 μW, 887 mV, 748 μA and 75 minutes respectively.

Keywords: Bromocresol, EDTA, Tween 80, Photogalvanic effect (PGE), fill factor, power point, conversion efficiency.

1. Introduction :

The sun's energy is converted into electricity using solar power. Electricity and heat are two types of sun-generated energy and both are produced using solar panels that range in size from residential roofs to large-scale 'solar farms' covering hundreds of acres of rural land. Solar energy is solar radiation that may produce heat, cause chemical processes, or generate electricity. The overall quantity of solar energy incident on Earth exceeds the world's present and projected energy needs by a large margin. One of the key components for the nation's economic growth is energy. Massive dependency on conventional energy sources causes an increase in greenhouse gas emissions, such as carbon dioxide (CO_2), which worsens global

warming and threatens biodiversity. As a result, the environmental problem and the energy crisis are intimately creates. It is well to remember that a shortage of energy is a minor inconvenience to us, but for people in poorer countries it is a matter of life and death. The world energy demand is increasing due to population growth and to rising living standards.[1]

Energy that is produced by natural processes and constantly replenished is known as renewable energy. Solar energy is universal, decentralized, non-polluting, freely available energy source and essential for every kind of living organism. Photogalvanic cell an important device that provides desirable route for conversion of solar energy into electrical energy. It is a third type of photoelectrochemical cell which is used for solar energy conversion.[2] In PG cell two inert electrodes are used and the light is absorbed by the electrolytic dye solution. An electron transfer occurs between the excited photo sensitizer dye molecules and electron donor or acceptor molecules added to the electrolyte. A photovoltage between the two electrodes is developed if the light is absorbed by the electrolytic solution. Accordingly, the PG cell is essentially a concentration cell and is based on some photochemical reaction, which gives rise to high energy products on excitation by a photon. This energy product loose energy electrochemically lead to generate the electricity called as a photogalvanic effect (PGE). First of all this effect was observed in equilibrium of ferrous ferric iodine iodide but this effect was systematically investigated in Thionine-Fe system.[3-6] Thionine has been condensed with poly (N-methylolacrylamide) to give a polymer-dye complex. Depending on the polymer-dye ratio, a longer wavelength shift (red shift) is observed as compared to the spectrum of free thionine. Potential of photogalvanic is found to depend strongly on the polymer-dye ratio. [7] The photo potential and current in PG cell containing toluidine blue and reductant, Fe (II), EDTA, triethanolamine and triethylamine have been determined. The power output with EDTA or amines as reductant were higher than Fe (II). The efficiency of the EDTA-Toluidine blue PG cell has been estimated to be about 0.0022 percent. The photoelectrochemical behaviour of toluidine blue in the presence of reductant has been examined by cyclic voltametry.[8] PG cells may play an important role in direct conversion of solar energy to electrical energy by some photochemical reactions. A number of PG systems have been fabricated with the aim of obtaining higher power output. A few among the studied PG systems with their maximum photopotential are: thionine-Fe ion aqueous system 250 mV, proflavine-EDTA aqueous system 476 mV and tolusafranine-EDTA aqueous system 844 mV. Authors have reported a photopotential 615 mV in a redox system consisting of phenosafranine and EDTA in aqueous medium and this value increases with increasing temperature attaining 870 mV.[9] PG cells using toluidine blue-diethylenetriamine penta acetic acid and Methylene blue-EDTA have been developed. The effects of different parameters like pH, concentration, temperature, electrode area, diffusion length etc on the electrical output of the cell were studied. Current-voltage (i-V) characteristics and performance

of the cell were determined.[10-11] Gangotri K.M. et al have increased the electrical output as well as storage capacity up to reasonable mark by using various photosensitizer with micelles in photogalvanic cell.[12-13] PGE was studied in a PG cell containing ALS, ascorbic acid and Azur-A as a surfactant, reductant and photosensitizer, respectively. The effects of different parameters on the electrical output of the cell were observed. The observed conversion efficiency and storage capacity for this system were 0.5461 % and 110 minutes, respectively.[14] Genwa and Singh[15-16] have reported reasonable values of electrical output with different dyes i.e. Brilliant Blue and Lissamine green-B as photosensitizers in PG cells for solar power generation and storage. The PGE of Xylidine ponceau dye was studied in Xylidine ponceau–Tween 60–Ascorbic acid system. Cell generates maximum power of 68.77 µW in ideal conditions. Conversion efficiency was calculated by photo potential and current values at power point.[17] Modified PG cell for increasing the power and storage capacity have studied in EDTA- Safranine O-ALS system. This cell showed greatly enhanced performance in terms of charging time forty minutes, equilibrium photocurrent 1700 µA, power 364.7 µW and conversion efficiency (8.93 percent).[18] The PGE observed by Gangotri and Mohan[19-20] in Trypan blue- Arabinose and Nile blue- Arabinose PG cell systems cells. PGE also observed in spinach extract as photo-sensitizer for solar energy conversion and storage. The observed cell performance (charging time 18 minutes, V_{oc} 1050 mV, I_{sc} 1750 µA, storage capacity as half change time 44 minutes and conversion efficiency ≈ 9.22 percent) was very encouraging to photogalvanics.[21] An investigation on the photogalvanic effect was carried out by Rathore and Singh[22] using a Janus green B-DSS-EDTA system. As a reductant, EDTA is employed in this process, while the azo dye Janus green B is used as photo sensitizers. At its power point, the system is capable of producing power equal to 164.1 microwatts. The fill factor for the system is 0.33, while the system's conversion efficiency is 1.58%. In the dark, the cell operates for 180 minutes. The scientific society has used different photosensitizers, surfactants, reductants in PG cells for conversion of solar energy into electrical energy but no attention has been paid to the use of this system containing Bromocresol green dye, Tween 80 and EDTA chemicals as energy material to enhance the power output and performance of the PG cell. Therefore, the present work was undertaken to obtain better performance and commercial viability of the PG cell.

2.   Result and Discussion :

(a)   Effect of variation of Bromocresol green, EDTA and Tween 80 concentration :

The impact of variation of Bromocresol green, EDTA and Tween 80 concentration are given in table 1. The changes in dye concentration were also studied by using solution of Bromocresol green at different concentrations. It was observed that the photopotential, photocurrent and power increased with increasing in

concentration of the Bromocresol green. Maximum values of electrical output were obtained for a particular value of Bromocresol green concentration (2.3 x 10^{-5}M), above which a decrease in electrical output of the PG cell was observed. Low electrical output observed at the minimum concentration range of dye due to limited number of Bromocresol green molecules to absorb the major part of the light in the path, while higher concentration of Bromocresol green again resulted in a decrease in electrical output because intensity of light reaching to those dye molecules which are near to the electrode decreases due to absorption of the major portion of the light by the Bromocresol green molecules present in the path. Therefore corresponding fall in the electrical output. With increasing the concentration of the EDTA, photopotential, current and power were found to increase till it reaches a maximum value at 1.8 x 10^{-3} M. These values are 760.0 mV, 748.0 µA and 568.48 µW respectively. On further increase in concentration of EDTA, a decrease in the electrical output of the cell was observed. The fall in power output was also resulted with decrease in concentration of EDTA due to less number of molecules available for electron donation to the Bromocresol green dye. On the other hand, the movement of dye molecules hindered by the higher concentration of the EDTA to reach the electrode in the desirable time limit and it will also result into a decrease in electrical output. The electrical output of the cell was increased on increasing the concentration of Tween 80. A maximum (760.0 mV, 748.0 µA and 568.48 µW) result was obtained at a certain value (1.3 x 10^{-3} M) of concentration of Tween 80. On further increasing the surfactant concentration it react as a barrier and major portion of the surfactant photobleach the less number of dye molecules so that a down fall in electrical output was observed.

Table -1. Effect of variation of Bromocresol green , EDTA and Tween 80 concentrations Light Intensity = 10.4 mW cm^{-2} , Temperature = 303 K , pH = 11.69			
Concentrations **[Bromocresol green]×10^{-5} M**	**Photopotential (mV)**	**Photocurrent (µA)**	**Power (µW)**
2.1	642.0	617.0	396.11
2.2	722.0	681.0	491.68
2.3	760.0	748.0	568.48
2.4	723.0	689.0	498.14
2.5	643.0	582.0	374.22
[EDTA] x 10^{-3} M			
1.6	607.0	603.0	362.72

1.7	791.0	664.0	509.29
1.8	760.0	748.0	568.48
1.9	707.0	653.0	494.32
2.0	622.0	549.0	369.48
[Tween 80] x 10^{-3} M			
1.1	655.0	632.0	413.96
1.2	724.0	731.0	529.24
1.3	760.0	748.0	568.48
1.4	736.0	713.0	524.77
1.5	669.0	646.0	432.17

(b) **Effect of variation of pH**

PG cell containing Bromocresol green B-EDTA-Tween-80 System was found to be quite sensitive to pH of the solution. It was studied that there is an increase in the electrical output of the system on increases the pH. At pH 11.69 a maxima was obtained in photopotential, photocurrent and power (760.0 mV, 748.0 µA and 568.48 µW). On further pH increases, there was a decrease in electrical output. The optimum electrical output was obtained at particular pH value; it may be due to better availability of ascorbic acid in donar form at that pH value. The results showing the impact of pH are represented in the table 2.

Table –2 Effect of Variation of pH

Bromocresol green - EDTA-Tween-80 System	pH				
	11.59	**11.64**	**11.69**	**11.72**	**11.77**
Photopotential (mV)	634.0	725.0	760.0	721.0	639.0
Photocurrent (µA)	571.0	654.0	748.0	656.0	573.0
Power (µW)	362.01	474.15	568.48	472.98	366.15

(c) **Impact of diffusion length**

The impact of variation of diffusion length (it is distance between the two electrodes) on the current parameters of the cell (i_{max}, i_{eq} and initial rate of generation of photocurrent) was studied using H-shaped glass cells of different dimensions. It was observed that in the first few minutes of illuminations there is sharp increase in

the photocurrent. As consequences, the maximum photocurrent (i_{max}) increase in diffusion length because path for photochemical reaction was increased, but this is not observed experimentally whereas equilibrium photocurrent (i_{eq}) decreased linearly. Therefore, it may be concluded that the main electroactive species are the leuco or semi form of dye (photosensitizer) in the illuminated and dark chamber respectively. The ascorbic acid and its oxidation product act only as electron carriers in the path.

The results are given in table 3.

Table- 3 Effect of Diffusion Length

Diffusion Length D_L (mm)	40.00	45.00	50.00	55.00	60.00
Max^m Photocurrent in μA	755.0	756.0	758.0	760.0	763.0
Equilibrium Photocurrent in μA	751.0	750.0	748.0	746.0	743.0
Rate of initial Generation of Current in μA min^{-1}	19.87	19.89	19.95	20.00	20.08

(d)   Impact of light intensity

The effect of light intensity was studied by using intensity meter (Solarimeter model-501). It was found that photocurrent showed a linear increasing behaviour with the increase in light intensity whereas photo potential increases in a logarithmic manner. The impact of change in light intensity on the photo potential and current is graphically represented in figure 1.
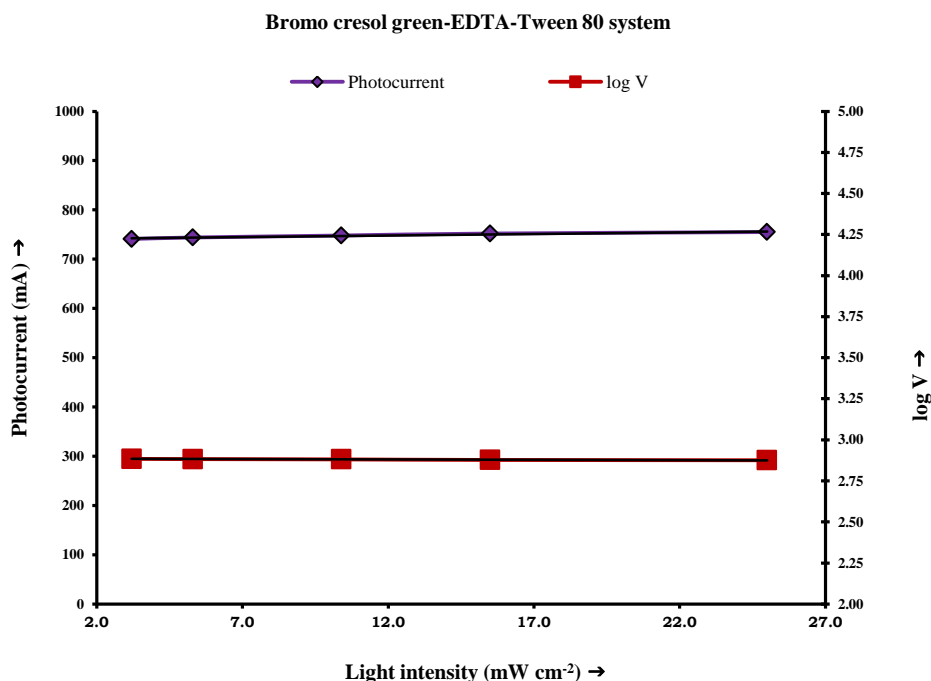
Fig. 1 VARIATION OF PHOTOCURRENT AND log V
WITH LIGHT INTENSITY

(e) Current-Voltage (i-V) properties of the cell

The short circuit current (i_{sc}) 748 µA and open circuit voltage (V_{oc}) 760 mV of the PG cell were measured with the help of a microammeter (keeping the circuit closed) and with a digital pH meter (keeping the circuit open), respectively. The photo current and potential values in between these two extreme values were recorded with the help of a carbon pot (log 470 K) connected in the circuit of multimeter, through which an external load was applied. The i-V properties of the PG cell containing Bromocresol green, EDTA and Tween 80 chemicals are graphically shown in figure 2. It was observed that i-V curve deviated from its regular rectangular shape. A point in the i-V curve, called power at point (pp), was determined where the product of photo current (i_{pp}) 190 µA and potential (v_{pp}) 527 mV was maximum. With the help of i-V curve, the fill-factor was reported 0.1509 by using the formula :

$$FF = \frac{Vpp \times Ipp}{Isc \times Voc}$$
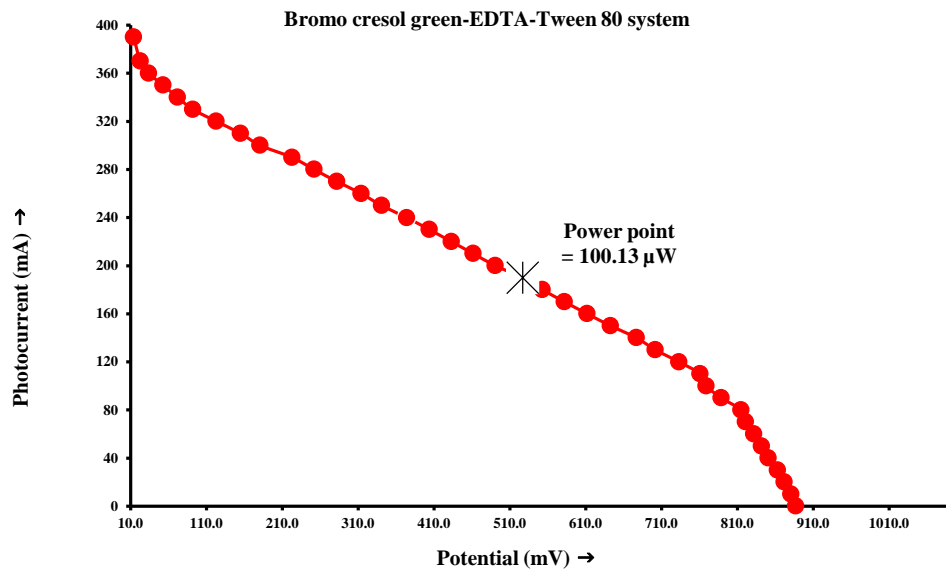
**Fig. 2 CURRENT VOLTAGE (i-V) CURVE
OF THE CELL**

(f)   Cell performance and conversion efficiency

The performance of the PG cell was observed by applying an external load (necessary to have current at power point) after terminating the light source as soon as the potential reaches at a constant value. The performance was determined in terms of $t_{1/2}$, i.e., the time required in fall of the power output to its half at power point in dark. It was observed that the cell containing Bromocresol green - EDTA - Tween 80 System can be used in dark for two hours. With the help of photo current and potential values at power point and the incident power of radiations, the conversion efficiency of the cell was determined as 0.96 % using the formula.

The results are graphically represented in time-power curve (figure 3).

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{A \times 10.4 mWcm^{-2}} \times 100\%$$
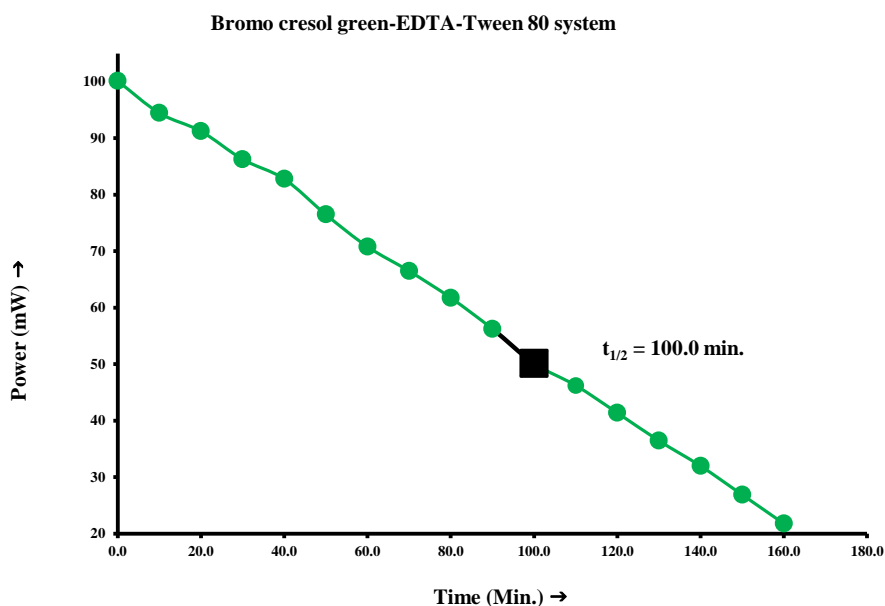
Fig. 3 TIME-POWER CURVE OF THE CELL

3. Mechanism :

When the dye molecule is excited by the light in the presence of electron donating substance (ascorbic acid), the dye rapidly changed into colorless form. The dye now acts as a powerful reducing agent and can donate electron to other substance and reconverted to its oxidized state. On the basis of earlier studies a tentative mechanism in PG cell shown in figure 4.
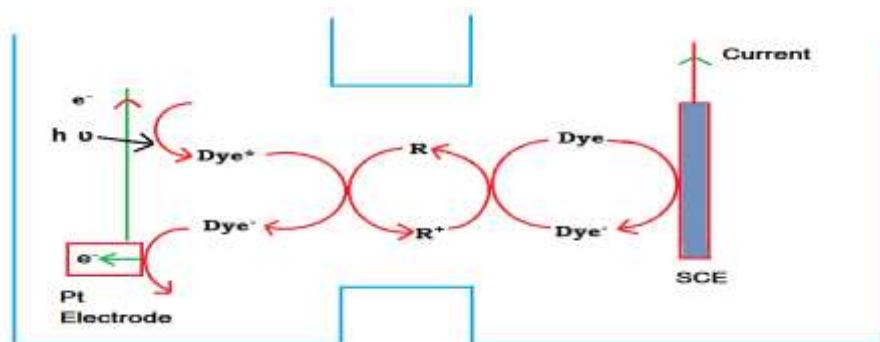

Fig. 4 Scheme of mechanism

SCE = Saturated calomel electrode   D = Dye (Photosensitizer)

R = Reductant   D = Semi & Leuco form

4.   Materials and methods :

Bromocresol green, EDTA, Tween 80 and NaOH of Loba Chemie were used in the present work. Solutions of EDTA, Bromocresol green, Tween 80 and NaOH (1N) were prepared in double distilled water (conductivity 3.5×10^{-5} Sm^{-1}) and kept in amber coloured containers to protect them from sun light. A solution of Bromocresol green, EDTA, Tween 80 and NaOH was taken in an H–type glass tube which was blackened by black carbon paper to protect from sun light. A shiny Pt foil electrode (1.0×1.0 cm^2) was immersed in one limb of the H–tube and a saturated calomel electrode (SCE) was immersed in the other limb. Pt-electrode acts as a working electrode and SCE as a counter electrode. The whole system was first placed in the dark till a stable potential was attained, then the limb containing the Pt-electrode was exposed to a 200 W tungsten lamp (Philips). A water filter was used to cut off thermal radiation. A digital multimeter (HAOYUE DT830D Digital Multimeter) was used to measure the photo potential and current generated by the system respectively. The i-V characteristics were studied by applying an external load with the help of Carbon pot (log 470 K) connected in the circuit the PG cell set-up is shown in figure 5.
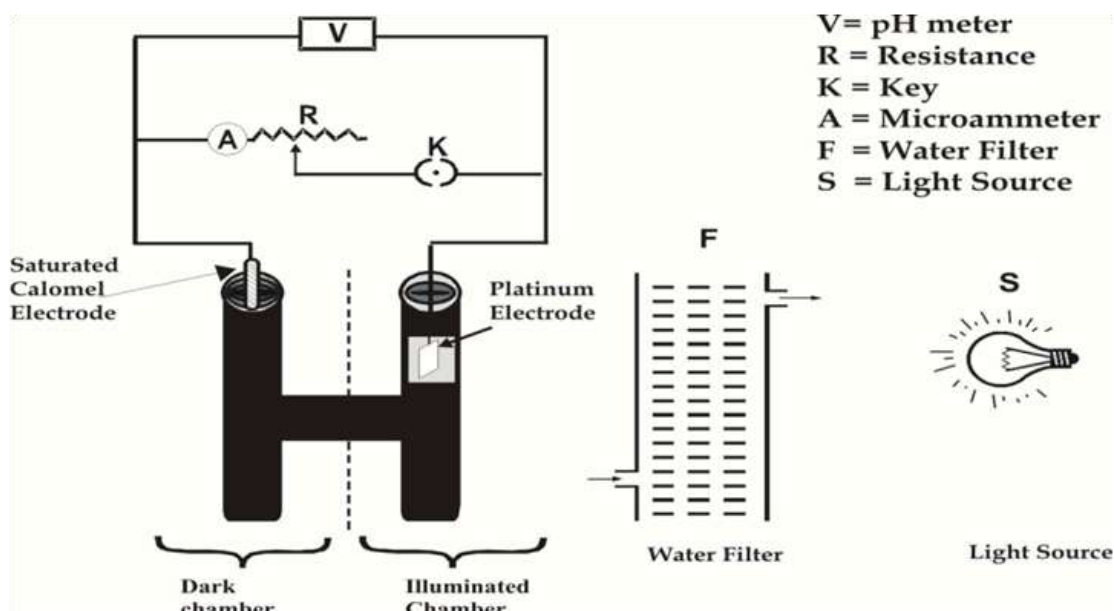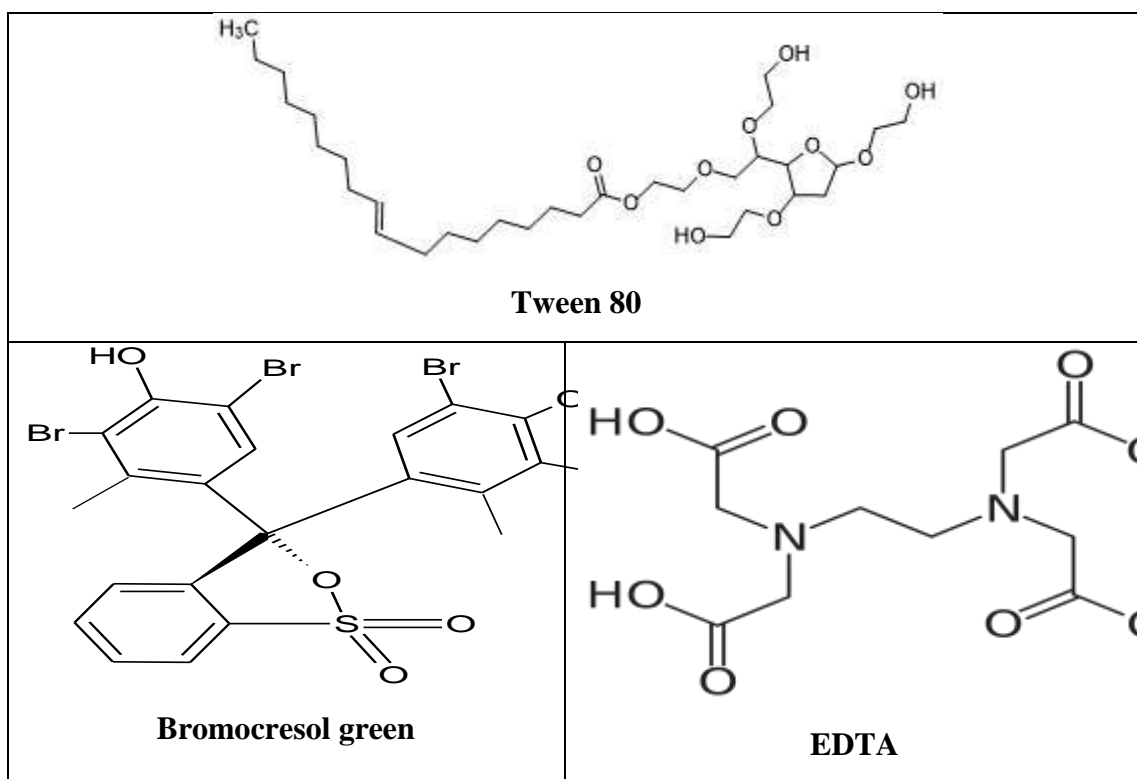

Fig.5 Photogalvanic Cell Set-up

Tween 80

Bromocresol green

EDTA

Structures of chemicals

5.   Conclusions :

The PG cell have inbuilt storage capacity and stored energy can be used in absence of light whereas photovoltaic cell needs extra hardware as battery for energy storage, PG cells are favourable than photovoltaic cells because low cost materials are used in this system. The conversion efficiency, storage capacity, power at power point and fill factor are recorded as 0.96 %, 100 minutes, 100.13 µW and 0.1509 respectively in Bromocresol green - EDTA - Tween 80 System.

Acknowledgement

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