Significance of Aniline blue in liquid phase dye sensitized Photo Galvanic cell for Solar power generation and Storage by using Ascorbic acid and Sodium Lauryl Sulphate chemicals

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Abstract

A primary source of renewable energy is solar energy. This is the one of the most resourceful sources of energy for the future. The photogalvanic cells as described in the present work are energy devices as they provide a route for simultaneous solar power generation and its storage. The study of photogalvanics of Aniline blue dye (photo-sensitizer)- Ascorbic acid (reductant)-Sodium Lauryl Sulfate (surfactant) has been done in basic medium at low intense light with aim of searching relatively proper combination of chemicals like photosensitizer, reductant and surfactant for further increasing the efficiency of these cells.

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 and equilibrium current at 10.4 $mWcm^{-2}$ have been observed of the order of 2.31%, 0.2445, 130 min, 240.24 μW, 1485 mV and 750μA respectively.

Keywords: Aniline blue, ascorbic acid, sodium lauryl sulphate (NaLS), photogalvanic effect, fill factor, power point, conversion efficiency.

Introduction

The world demand for energy is rapidly increasing and there is a need of energy to warm our homes, to cook our meals, to travel, communicate, to power our factories and other developmental processes. The amount of energy available to us determines not only our standard of living, but also how long we live. Detailed statistics from many countries shows that in countries where the available energy is 0.15 tons of coal equivalent per person per year, the average life expectancy is about forty years, whereas in America and Europe, the available energy is hundred times greater, people have an average life expectancy of about seventy-five years.

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.[12] Solar energy is universal, decentralized, non-polluting, freely available energy source and essential for every kind of living organism. Photogalvanic cell is 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.[3]

In photogalvanic cell, two inert electrodes are used and the light is absorbed by the electrolyte, for instance, a dye solution. An electron transfer occurs between the excited 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 electrolyte. Accordingly, the photogalvanic cell is essentially a concentration cell and is based on some chemical reaction, which gives rise to high energy products on excitation by a photon. This energy product loses energy electrochemically to generate the electricity called as a photogalvanic effect.

First of all the photogalvanic effect was observed in equilibrium of ferrous ferric-iodine iodide but this effect was systematically investigated in thionine-Iron system.[13,16-18] Thionine has been condensed with poly (N-methylolacrylamide) to give a polymer-dye complex. Spectral and photogalvanic properties of the complex have been studied. Depending on the polymer-dye ratio, a bathochromic shift is observed as compared to the spectrum of free thionine. Photogalvanic potential is found to depend strongly on the polymer-dye ratio.[20]

The photovoltages and photocurrents in photogalvanic cells containing toluidine blue (Tb) and reducing agents, Fe (II), EDTA, triethanolamine and triethylamine have been determined. The photo outputs with EDTA or amines as reducing agents were higher than Fe (II). The efficiency of the EDTA-Tb photogalvanic cell has been estimated to be about 0.0022%. The electrochemical behaviour of toluidine blue in the presence of all the reducing agents has been examined by cyclic voltametry[15].

Photogalvanic cells may play an important role in direct conversion of solar energy to electrical energy by chemical means. A number of systems have been proposed and studied with the aim of obtaining higher photovoltage and photocurrent. A few among the studied systems with their maximum photovoltages are: thionine-ferrous ion aqueous system 250 mV, proflavine-EDTA aqueous system 476 mV and tolusafranine-EDTA aqueous system 844 mV.

Rohtagi et al[19] have reported a photovoltage 615 mV in a redox system consisting of phenosafranine and EDTA in aqueous medium and this value increases with increasing temperature attaining 870 mV. Photogalvanic cells using toluidine blue diethylenetriamine penta acetic acid (TB - DTPA) 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 observed. Current-voltage (i-v) characteristics and performance of the cell were determined.[1,2] Gangotri et al[4,5] have increased the electrical output as well as storage capacity up to reasonable mark by using various photosensitizer with micelles in photogalvanic cell. Photogalvanic effect was studied in a photogalvanic cell containing NaLS–ascorbic acid and Azur A as a surfactant, reductant and photosensitizer respectively. The photopotential (770mV), photocurrent (160μA) and the effect of different parameters on the electrical output of the cell were observed and current–voltage characteristics of the cell have also been studied.

The observed conversion efficiency and storage capacity for this system were 0.5461 and 110.0min respectively[7]. Genwa and Singh[9-11] have reported reasonable values of electrical output with different dyes i.e. Brilliant Blue-FCF (BB-FCF), Lissamine green-B (LGB) and Bromocresol green (BCG) as photosensitizers in photogalvanic cells for solar energy conversion and storage.

The photogalvanic behaviour 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 photopotential and photocurrent values at power point[8].

Modified photogalvanic cell for enhancing the solar power generation and storage was studied with EDTA, Safranine O and NaLS chemicals. This cell showed greatly enhanced performance in terms of charging time (40 min), initial generation of photocurrent (260 μA min^{-1}), equilibrium photocurrent (1700 μA), power (364.7 μW) and efficiency (8.93%).[6] Photogalvanic effect was also observed in spinach extract as photo-sensitizer for sun light conversion and storage.

The observed cell performance (charging time 18 min, open-circuit potential 1050 mV, short-circuit current 1750 μA, storage capacity as half change time 44 min and efficiency ≈ 9.22%) were very encouraging to photogalvanics[14]. The scientific society has used different photosensitizers, surfactants, reductants in photogalvanic cells for conversion of solar energy into electrical energy but no attention has been paid to the use of this system containing aniline blue dye as energy material to increase the electrical output and performance of the photogalvanic cell. Therefore, the present work was undertaken to obtain better performance and commercial viability of the photogalvanic cell.

Material and Methods

Aniline blue (Ases Chemical, Jodhpur), ascorbic acid (Ases Chemical, Jodhpur), NaLS (Sisco Research Laboratories, Mumbai) and NaOH (RFCL, New Delhi) were used in the present work. Solutions of ascorbic acid, aniline blue, NaLS 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. Aniline blue dye (Scheme 1) is dark brown-purple crystal with metal luster, soluble in water and stable under normal temperature and pressure. Its molecular formula and molecular weight are: $C_{32}H_{25}N_3Na_2O_9S_3$ and 737.73 $g \cdot mol^{-1}$ respectively.

A mixture of solutions of dye, reductant, surfactant and NaOH was taken in an H–type glass tube which was blackened by black carbon paper unaffected from sun radiation. A shiny platinum foil electrode (1.0 x 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. Platinum 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 platinum electrode was exposed to a 200 W tungsten lamp (Philips). A water filter was used to cut off thermal radiation. Photochemical bleaching of the dye was studied potentiometrically.

A digital multimeter (HAOYUE DT830D Digital Multimeter) was used to measure the potential and current generated by the system respectively. The current voltage characteristics were studied by applying an external load with the help of carbon pot (log 470 K) connected in the circuit the photogalvanic cell set-up is shown in figure 5.

Results and Discussion

Effect of variation of Aniline blue, ascorbic acid and NaLS concentration: The effect of variation of Aniline blue, ascorbic acid and NaLS concentration are given in Table 1. Variation of dye concentration studied by using solution of Aniline blue of different concentrations. It was observed that the photopotential, photocurrent and power enhanced with enhancing in concentration of the dye [Aniline blue]. A maximum (at 1485 mV, 750μA and 982.50 μW) was obtained for a particular value of dye concentration (2.1 x 10^{-5}M), above which a decrease in electrical output of the cell was observed.

Low electrical output was observed at the minimum concentration range of dye due to limited number of dye molecules to absorb the major part of the light in the path, while higher concentration of dye again resulted in a decrease in electrical output because intensity of light reaching the molecule near the electrode decreased due to absorption of the major portion of the light by the dye molecules present in the path.

Table 1
Effect of variation of Aniline Blue, ascorbic acid and NaLS concentrations
Light Intensity = 10.4 mW cm^{-2}, Temperature = 303 K, pH = 11.70

Concentrations	**Photo potential (mV)**	**Photocurrent (μA)**	**Power (μW)**
[Aniline blue]× 10^{-5} M			
2.0	1156.0	605.0	699.38
2.2	1208.0	680.0	821.44
2.6	1310.0	750.0	982.50
2.8	1250.0	685.0	856.25
3.0	1160.0	598.0	693.68
[Ascorbic acid] x 10^{-3} M			
1.7	1165.0	525.0	611.63
1.9	1265.0	645.0	815.93
2.1	1310.0	750.0	982.50
2.4	1244.0	632.0	786.21
2.6	1154.0	534.0	616.24
[NaLS] x 10^{-3} M			
1.7	1128.0	524.0	591.07
1.9	1188.0	652.0	774.58
2.2	1310.0	750.0	982.50
2.4	1225.0	658.0	806.05
2.7	1100.0	512.0	563.20

Therefore, there was a corresponding fall in the electric output. With the increase in concentration of the reductant [ascorbic acid], the photopotential, photocurrent and power were found to increase till they reach a maximum value at 2.1 x 10^{-3} M as 1485 mV, 750µA and 982.50 µW respectively. On further increase in concentration of ascorbic acid, a decrease in the electrical output of the cell was observed. The fall in power output also resulted with decrease in concentration of reductant due to less number of the molecules available for electron donation to the cationic form of dye.

On the other hand, the movement of dye molecules was hindered by the higher concentration of the reductant to reach the electrode in the desired time limit to result in to a decrease in electrical output. The electrical output of the cell was increased on increasing the concentration of surfactant [NaLS]. A maximum (1485 mV, 750µA and 982.50 µW) result was obtained at a certain value (2.2 x 10^{-3}M) of concentration of NaLS. On further increasing the surfactant concentration, it reacted as a barrier and major portion of the surfactant photobleaches the less number of dye molecules, so that a down fall in electrical output was observed.

Effect of variation of pH: Photogalvanic cell containing Aniline blue – Ascorbic acid –NaLS system was found to be quite sensitive to pH of the solution. It was observed that there is an increase in the photopotential, photocurrent and power of the system with the increase in pH value (in the alkaline range). At pH 11.70, a maxima was obtained (1485 mV, 750 µA and 982.50 µW).

On further increase in pH, there was a decrease in photopotential, photocurrent and power. The optimum electrical output was obtained at particular pH value. It may be due to better availability of reductants donar form at that pH value. The results showing the effect of pH are summarized in the table 2.

Effect of diffusion length: The effect 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 cells of different dimensions. It was observed that in the first few minutes of illuminations, there is sharp increase in the photocurrent. As a consequence, the maximum photocurrent (i_{max}) increase in diffusion length was observed because path for photochemical reaction was increased, but this is not observed experimently whereas equilibrium photocurrent (i_{eq}) decreased linearly.

Therefore, it may be concluded that the main electroactive species are the leuco or semi forms of dye (photosensitizer) in the illuminated and dark chamber respectively. The reductant and its oxidation products act only as electron carriers in the path. The results are summarized in table 3. The effect of electrode area on the current parameters of the cell was also studied. It was observed that with the increase in the electrode area, the value of maximum photocurrent (i_{max}) is found to increase. The results are summarized in table 4.

Effect 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 photopotential increases in a logarithmic manner. This increase is in number of photons with increase in light intensity. The effect of variation of light intensity on the photopotential and photocurrent is graphically represented in fig. 1.

Current-Voltage (i-V) characteristics of the cell: The short circuit current (i_{sc}) 750 µA and open circuit voltage (V_{oc}) 1310 mV of the photogalvanic 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 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 characteristics of the photogalvanic cells containing Aniline blue –Ascorbic acid –NaLS system is graphically shown in fig. 2 and summarized in table 5. It was observed that i-V curve deviated from its regular rectangular shape. A point in the i-V curve, called power point (pp), was determined where the product of curve of current (i_{pp}) 330 µA and potential (v_{pp}) 728 mV was maximum. With the help of i-V curve, the fill-factor was calculated as 0.2445 using the formula:

$$\text{Fill factor } (\eta) = \frac{\text{Vpp x ipp}}{\text{Voc x isc}} \qquad (1)$$

Table 2
Effect of Variation of pH
[Aniline blue] = 2.6 x 10^{-5} M Light Intensity = 10.4 mW cm^{-2}
[Ascorbic acid] = 2.1 x 10^{-3} M Temperature = 303 K
[NaLS] = 2.2 x 10^{-3} M

pH	Photopotential (mV)	Photocurrent (µA)	Power (µW)
11.35	1122.0	515.0	577.83
11.55	1265.0	690.0	872.85
11.70	1310.0	750.0	982.50
11.80	1255.0	695.0	872.23
11.95	1124.0	510.0	573.24

Table 3
Effect of Diffusion Length and electrode area
[Aniline Blue] = 2.6 x 10^{-5} M Light Intensity = 10.4 mW cm^{-2}
[Ascorbic acid] = 2.1 x 10^{-3} M Temperature = 303 K
[NaLS] = 2.2 x 10^{-3} M pH = 11.70

Diffusion Length DL (mm)	Maximum Photocurrent imax (µA)	Equilibrium Photocurrent ieq (µA)	Rate of initial Generation of Current (µA min^{-1})
35	800.0	758.0	21.05
40	805.0	754.0	21.18
45	810.0	750.0	21.32
50	820.0	746.0	21.58
55	828.0	742.0	21.79

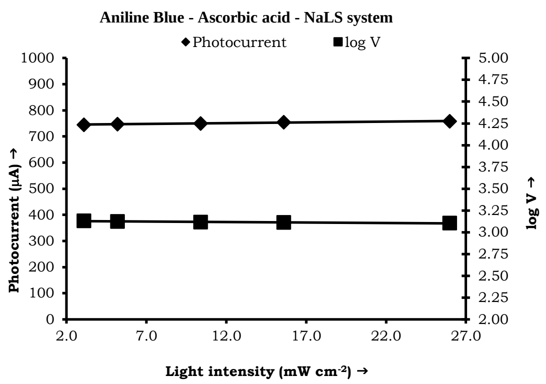


Fig. 1: Variation of Photocurrent and log V with Light Intensity

Table 4
Effect of Electrode Area

[Aniline Blue] = 2.6 x 10^{-5} M   Light Intensity = 10.4 mW cm^{-2}
[Ascorbic acid] = 2.1 x 10^{-3} M   Temperature = 303 K
[NaLS] = 2.2 x 10^{-3} M   pH = 11.70

Electrode Area (cm^2)	**Maximum photocurrent i_{max} (μA)**	**Equilibrium photocurrent i_{eq} (μA)**
0.70	795.0	755.0
0.85	800.0	752.0
1.00	810.0	750.0
1.15	826.0	742.0
1.30	832.0	735.0

Table 5
Current-Voltage (i-V) characteristics of the cell

[Aniline Blue] = 2.6 x 10^{-5} M   Light Intensity = 10.4 mW cm^{-2}
[Ascorbic acid] = 2.1 x 10^{-3} M   Temperature = 303 K
[NaLS] = 2.2 x 10^{-3} M   pH = 11.70

Potential (mV)	**Photocurrent (μA)**	**Fill Factor (η)**
1485	0	
1422	5	
1400	10	
1395	15	
1333	20	
1304	25	
1278	30	
1256	40	
1212	50	
1185	60	
1158	75	
1130	95	
1104	105	
1078	115	
1052	125	
1028	135	
992	155	
952	170	
945	180	
894	210	
788	270	
764	280	
762	285	
746	315	
732	325	
728	**330**	**0.2445**
680	340	
580	375	
566	388	
452	430	
445	440	
400	465	
390	480	
340	505	
240	580	
196	610	
185	620	
80	720	
0	750	

Cell performance and conversion efficiency: The performance of the photogalvanic cell was observed by applying an external load (necessary to have current at power point) after terminating the illumination as soon as the potential reaches a constant value. The performance was determined in terms of $t_{1/2}$ i.e. the time required in fall of the output (power) to its half at power point in dark. It was observed that the cell containing Aniline blue - Ascorbic acid - NaLS can be used in dark for 130.0 minutes. With the help of current and potential values at power point and the incident power of radiations, the conversion efficiency of the cell was determined as 2.31% using the formula. The results are graphically represented in time-power curve (Fig. 3).

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{A \times 10.4 mWcm^{-2}} \times 100\% \qquad (2)$$

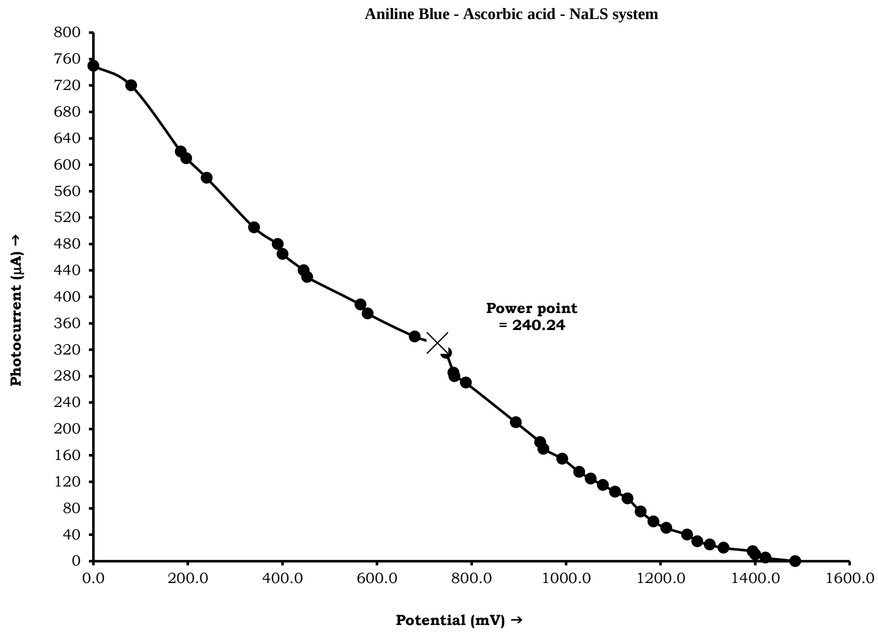


Fig. 2: Current Voltage (i-V) Curve of the Cell

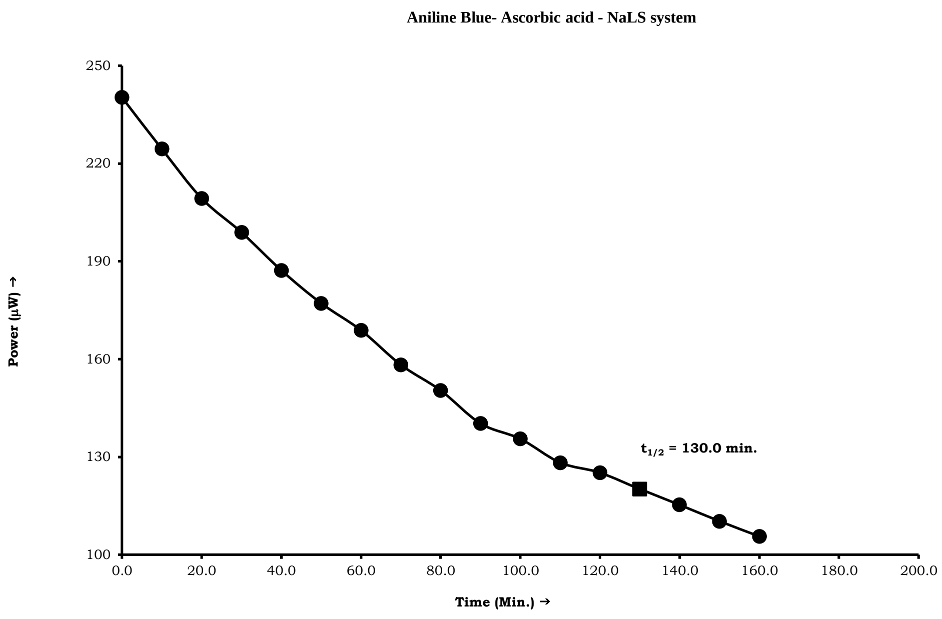


Fig. 3: Time-Power Curve of the Cell

Mechanism: When certain dyes are excited by the light in the presence of electron donating substance (reductant), the dyes are rapidly changed into colorless form. The dye now acts as a powerful reducing agent and can donate electron to other substance and is reconverted to its oxidized state. On the basis of earlier studies, a tentative mechanism in the photogalvanic cell may be proposed as follows:

Illuminated chamber: On irradiation, dye molecules get excited.

$$\text{Dye} \xrightarrow{h\upsilon} \text{Dye*} \qquad \text{(i)}$$

The excited dye molecules accept an electron from reductant and get converted into semi or leuco form of dye and the reductant into its excited form.

$$\text{Dye*} + \text{R} \longrightarrow \text{Dye}^{-}\ \text{(semi or leuco)} + \text{R}^{+} \qquad \text{(ii)}$$

At platinum electrode:

The semi or leuco form of dye loses an electron and converted into original dye molecule.

$$\text{Dye-} \longrightarrow \text{Dye} + e^{-} \qquad \text{(iii)}$$

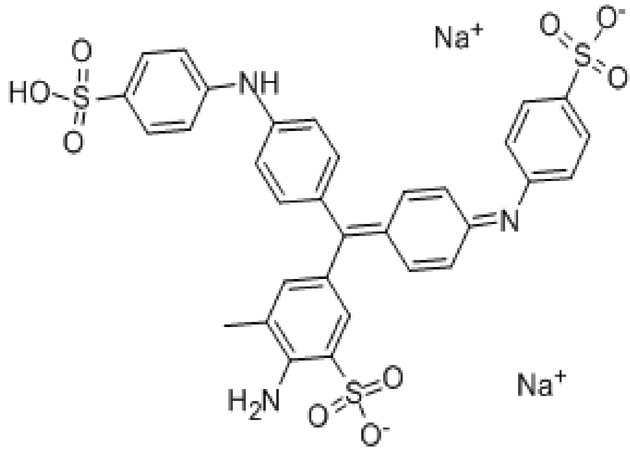
Dark Chamber:
At counter electrode:

$$\text{Dye} + \text{e-} \longrightarrow \text{Dye}^{-}\ \text{(Semi or leuco)} \qquad \text{(iv)}$$

Finally, leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule. This cycle of mechanism is repeated again and again leading to production of current continuously.

$$\text{Dye-} + \text{R+} \longrightarrow \text{Dye} + \text{R} \qquad \text{(v)}$$

Here Dye, Dye*, Dye-, R and R+ are the dye, its excited form, leuco form, reductant and its oxidized form respectively. The scheme of mechanism is shown in fig. 4.



Scheme 1: Aniline blue

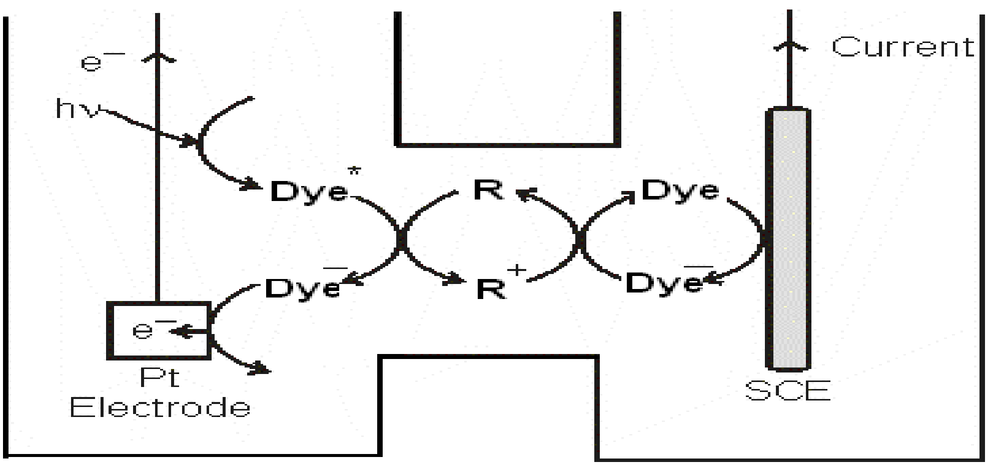


Fig. 4: Scheme of mechanism
SCE = Saturated calomel electrode D = Dye (Photosensitizer)
R = Reductant D = Semi & Leuco form

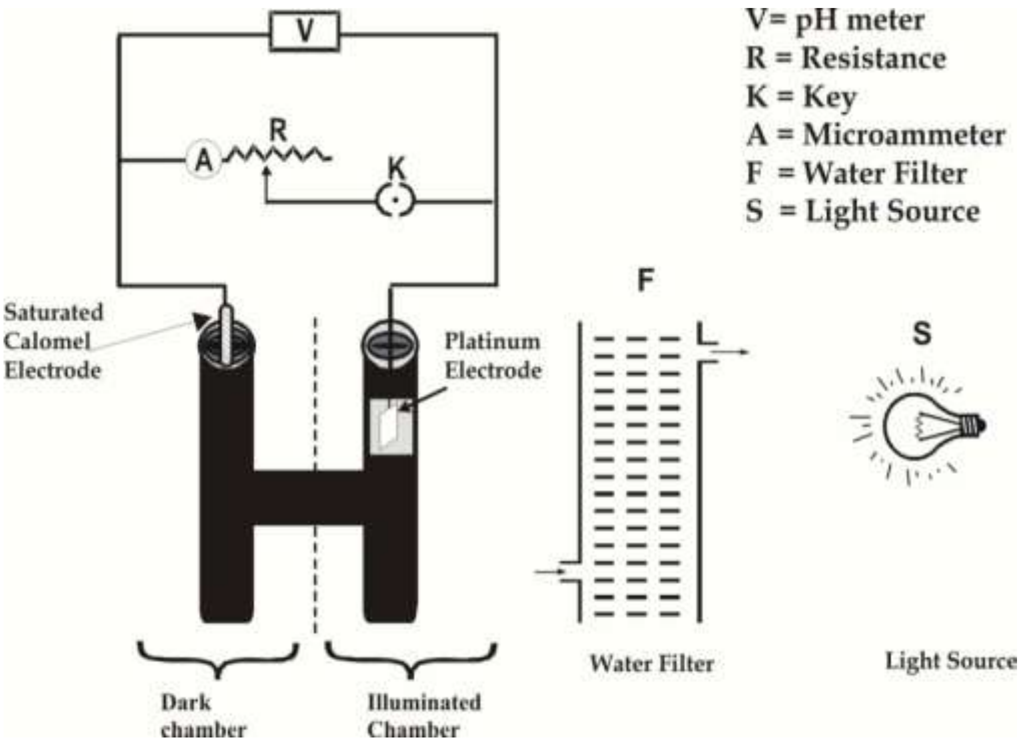


Fig. 5: Photogalvanic Cell Set-up

Conclusion

The photogalvanic cells 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; photogalvanic cells are favourable than photovoltaic cells because low cost materials are used in these cells.

The conversion efficiency, storage capacity, power at power point and fill factor are recorded as 2.31%, $t_{1/2}$ 130.0 min, 240.24 μW and 0.2445 respectively in Aniline blue - Ascorbic acid – NaLS system.

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