

# Energy efficiency, solar energy conversion and storage in photogalvanic cell

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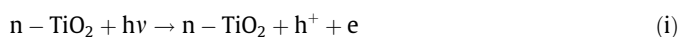
## ABSTRACT

Solar generating photogalvanic cell collect the energy from the sun for conversion to electricity. In the present work photogalvanic effect was studied in photogalvanic cell consisting Tween 60 – Biebrich scarlet – Ascorbic acid system. The photopotential, photocurrent and power generated in cell were 919.0 mV, 210.0  $\mu$ A and 93.15  $\mu$ W respectively. The conversion efficiency and storage capacity reported in this article as 0.8967% and 75.0 min. respectively. The effects of other parameters on the cell electrical output were investigated and a cell photoreaction mechanism for the generation of the photocurrent has also been proposed. The results also shown the efficiency along with storage performance of a photogalvanic cell based on Tween 60 – Biebrich scarlet – Ascorbic acid system.

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## 1. Introduction

The most important scientific and technical challenge facing humanity in the 21st century are energy security, environmental security and economic security; these can likely be met only through addressing the energy problem with in the next 10–20 years. Meeting global energy demand in a sustainable fashion will require not only increased energy efficiency and new methods of using existing carbon based fuels but also energy. Solar energy is to be a major primary energy source, utilization requires solar capture and conversion and storage [1]. Photoelectrosynthetic is an uphill chemical reaction using a solar energy photons so that solar energy is stored in the chemical, uphill meaning requires external energy to be given to the system for decomposition [2]. The water decomposition to hydrogen and oxygen is an uphill process solar energy is able to drive it using a semiconductor [3–7]



where  $h^+$  is a hole and  $e$  is the electron. This is followed by:



Solar energy is abundant and if used efficiently could produce the energy needed for a long time to come. In particular the solar thermal approach seems rather promising in the sense that it can

be made rather efficient, it use standard technologies for heat conversion and utilization and it has potentialities for a price competitive to other sources. An advanced photovoltaic may take over at a later date. However meaningful utilization of this form of energy is limited to the “sun belt” of relatively desert and sunny lands, fortunately of large proportion, but often very far of the main centers of human activities [8]. It requires the development of renovated system of energy carriers in which electricity and hydrogen are the main continents [9,10]. Albery and Archer [11] have studied optimum efficiency of photogalvanic cell for solar energy conversion. Buttler and Ginley [12] have explained principal of photoelectrochemical cell and Gerischer [13] studied on heterogeneous electrical system for solar energy conversion. Gratzel [14] reported the photoejection of electron in dye surfactant system in photovoltaic and photoelectrochemical conversion of solar energy. Vittal et al. [15] reported the use on beneficial role of surfactant in electrochemistry, Pokhrel and Nagaraja [16] have reported photogalvanic behavior of bound dyes on semiconductor surface of  $[\text{Cr}_2\text{O}_2\text{S}_2(1-\text{Pdct})_2(\text{H}_2\text{O})_2]$  in aqueous DMR. Studies on energy efficiency in dye sensitized nanocrystalline solar cells reported by Usmani [17]. Later on Gangotri and Co-worker reported some other photogalvanic systems [18,19]. Chouhan and Genwa have used the 3G filter in photogalvanic cell and studied storage and energy efficiency of cell in detail [20,21]. Yadav and Lal [22] reported the efficient solar energy conversion and storage through photogalvanic cell based on EDTA – Brilliant and fast green. Recently, some different photosensitizer based photogalvanic cells reported by some Indian photo chemists [23–27].

The review of literature reveals that many workers have studied the harvesting of solar energy in various forms of solar cells. The

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various dyes and surfactants have been used in photogalvanic cells but energy efficiency (conversion efficiency) of photogalvanic cell is still low. So the use of suitable photosensitizer (a dye) with reductant in photogalvanic cell is needed for higher electrical output and energy efficiency. Therefore, with the aim of getting higher energy efficiency of photogalvanic cell, the use of a new dye Biebrich scarlet in Tween 60 – Biebrich scarlet – Ascorbic acid system was planned. The variation of dye, surfactant and reductant and NaOH have been studied for finding the suitable composition of dye-surfactant and reductant for optimum performance of the cell.

## 2. Material and methodology

### 2.1. Materials

Biebrich scarlet (Scheme 1) is dark red powder, soluble in water, molecular formula is  $C_{22}H_{14}N_4Na_2S_2$  molecular weight is 556.9 and Maximum absorption ( $\lambda_{max}$ ) is 520 nm.

Tween 60 (Polyoxyethylene sorbitan monostearate) is a pale yellow semisolid liquid (Scheme 2), it is soluble in water, molecular formula is  $C_{24}H_{46}O_6(C_2H_4O)_n$  and molecular weight is 1312.

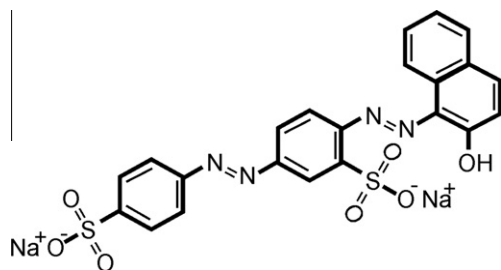
Ascorbic acid (Scheme 3) is a white to slightly yellowish crystalline powder soluble in water, its molecular formula is  $C_6H_8O_6$  and molecular weight is 176.13.

### 2.2. Absorption properties of Biebrich scarlet – Tween 60

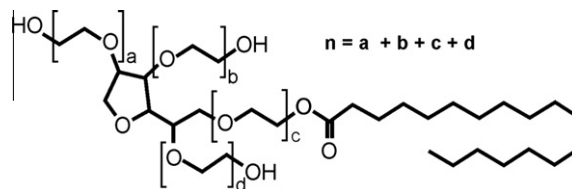
The spectral properties of Biebrich scarlet dye was studied and wavelength of maximum absorption intensity with the help of spectrophotometer. The dye observed absorption intensity ( $\lambda_{max}$ ) in visible region with maximum at 580 nm. Maximum absorption is recorded at Biebrich scarlet – Tween 60 combination of concentration  $4.8 \times 10^{-5} M + 1.2 \times 10^{-3} M$ . The changes in the spectra can be seen in Fig. 1.

### 2.3. Methods

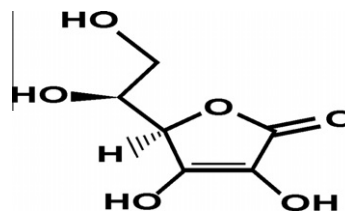
A dye Biebrich scarlet, Tween 60, Ascorbic acid and NaOH solution having concentrations  $4.8 \times 10^{-5} M$ ,  $1.2 \times 10^{-3} M$ ,  $2.08 \times 10^{-3} M$  and 1.0 N respectively, were used in present work. Photogalvanic effect of dye was studied using H-shaped glass tube which consist known amount of the solution of Biebrich scarlet, Tween 60, Ascorbic acid, NaOH and water so as to keep total volume of the mixture always 25.0 ml. A Platinum foil electrode ( $1.0 \times 1.0 cm^2$ ) was dipped in one limb and a saturated calomel electrode (SCE) is immersed in another limb of the H-tube. The terminals of the electrodes were then connected to a digital pH meter and the whole cell is placed in dark. The photopotential was measured in dark when the cell attains a stable potential. The limb containing platinum electrode was focused to the light source (projector Tungsten lamp). The light intensity was varied by employing tungsten lamp of 200 W and Solarimeter (Surya Sys-



Scheme 1.



Scheme 2.



Scheme 3.

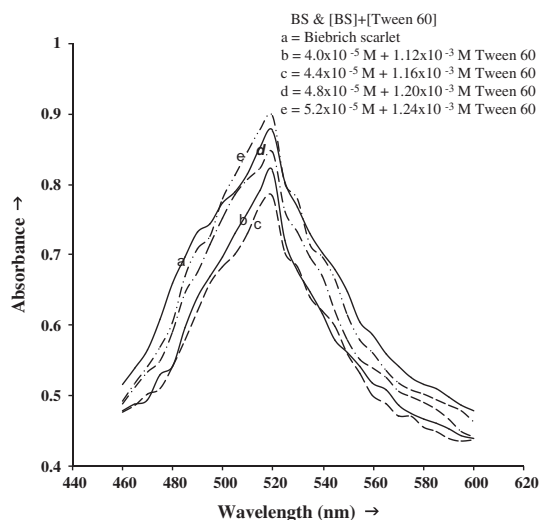


Fig. 1. Absorption spectrum of dye and Dye + Surfactant.

tems, Ahmadabad, India). A water filter was placed between the illuminated chamber and the light source to cut off thermal radiation. Photopotential and photocurrent were measured by digital pH meter (Systronics model 335, Ahmadabad, India) and digital ammeter (Osaw, Haryana, India). Absorption spectra were recorded using Systronics Spectrophotometer 106 with the matched pair of silica cuvettes (path length 1 cm). All spectral measurements were duplicated in a constant temperature water bath maintained with in  $\pm 1^\circ C$  and mean values were processed for data analysis. Over all experimental setup and circuit is shown in Fig. 2.

### 2.4. Mechanism

The mechanism of photosensitization approach for degrading dye molecule on  $TiO_2$  surface under visible light irradiation [28,29] is show as under:



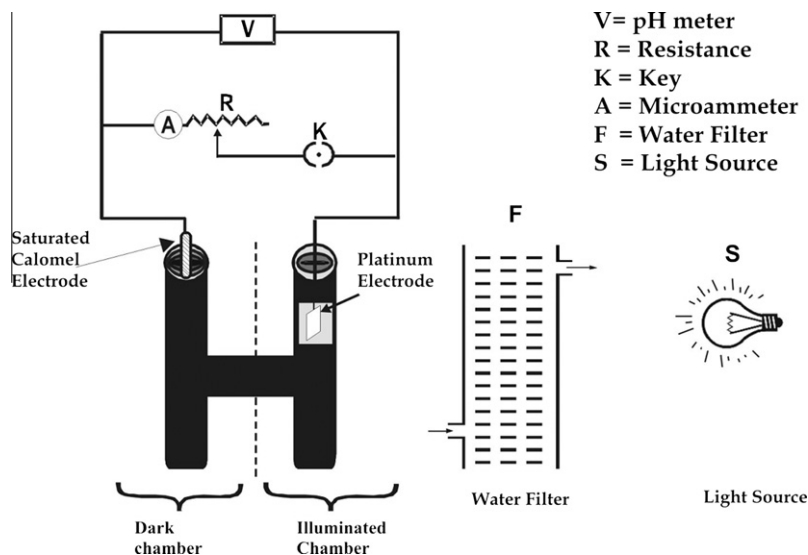
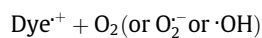


Fig. 2. Experimental circuit.



→ Peroxyleted or hydroxyleted

→ Degraded or mineralized product  
(ix)

where dye rather than  $\text{TiO}_2$  particles are excited by visible light.

The mechanism of photocurrent generation in photogalvanic cell may be proposed as follow:

On illumination, the dye molecule gets excited. The excited dye molecule accepts an electron from reductant and gets converted into semi or leuco form of dye. At platinum electrode, the semi or leuco form of dye loses an electron and converted into original dye molecule. At counter electrode (SCE, dark chamber), the dye molecules accept an electron from electrode and gets converted into semi or leuco form. Finally leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule and this cycle goes on in the cell [30]. The mechanism is schematically represented in Fig. 3. Both singlet and triplet excited state are involve here, but the triplet being relatively more stable then singlet state has role in storage capacity. Thus this cell can be used for solar energy conversion in electrical power (d.c. current) and storage of generated solar power.

The photogalvanic cell undergoes cyclical charging and discharging process. The charging of cell occurs only in presence of illuminating source. The discharging of cell takes place only when

we apply the external circuit for electron transfer. As long as there is no external circuit, the cell will keep light energy stored. For how long cell will store light energy depends on stability of excited state of dye and population of excited dye molecules. The storage capacity of the cell will be higher if excited dye molecules are more stable due to its bulkiness or amount of delocalization of excited electrons on it or if for any reason say, due to recombination of  $\text{D}^-$  and  $\text{R}^+$  as a result of diffusion, the concentration of dye is reduced, the storage capacity of cell is also reduced [31]. So, further research with a view to stop this recombination of  $\text{D}^-$  and  $\text{R}^+$  is a challenge for workers in future.

### 3. Results and discussion

#### 3.1. Effect of variation of dye (Biebrich scarlet), surfactant (Tween 60), and reductant (Ascorbic acid) concentration

Results showing the effect of dye, surfactant and reductant concentration are given in Table 1. It was observed that the photopotential and photocurrent of Tween 60 – Biebrich scarlet – Ascorbic

Table 1

Effect of variation of Biebrich scarlet, Tween 60 and Ascorbic acid concentration.

Concentration	Photopotential (mV)	Photocurrent ( $\mu\text{A}$ )
<i>(Biebrich scarlet) <math>\times 10^{-5} \text{ M}</math></i>		
4.0	786	179
4.4	856	194
4.8	919	210
5.2	836	182
5.6	762	168
<i>(Tween 60) <math>\times 10^{-3} \text{ M}</math></i>		
1.12	805	143
1.16	867	193
1.20	919	210
1.24	880	181
1.28	853	164
<i>(Ascorbic acid) <math>\times 10^{-3} \text{ M}</math></i>		
2.00	762	121
2.04	825	160
2.08	919	210
2.12	862	174
2.16	815	130

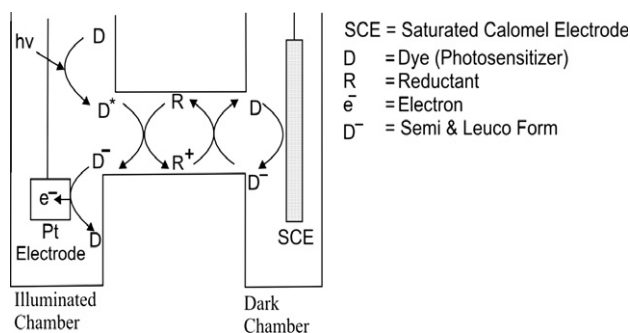


Fig. 3. Scheme of mechanism.

<sup>a</sup>Light intensity =  $10.4 \text{ mW cm}^{-2}$ ; <sup>b</sup>Temp. = 298 K; <sup>c</sup>pH = 10.69.

acid system for the better performance of the photogalvanic cell proper concentration of dye was needed. Experimentally, photopotential and photocurrent increased with Biebrich scarlet concentration. A maxima was obtained at certain dye concentration ( $4.8 \times 10^{-5}$  M). On further increase in dye concentration, a decrease in the electrical output was observed. On the lower concentration range of dye, there are limited numbers of dye molecules to absorb the major portion of the light in the path and therefore, there is minimum electrical output. A maximum photocurrent (250  $\mu$ A) and photopotential (919.0 mV) was generated at an optimum value of dye concentration ( $4.8 \times 10^{-5}$  M) at which maximum power was generated.

The nonionic surfactant Tween 60 was used as a surfactant in the cell system. The photopotential and photocurrent of the cell was increased on increasing the concentration of Tween 60. A maxima was obtained at a certain value ( $1.2 \times 10^{-3}$  M) and decreased on further increase in surfactant concentration. The most important properties of micellar systems are the ability to solubilize a variety of molecules and substantial catalytic effect on chemical reaction. With the increase in concentration of the reductant ( $2.08 \times 10^{-3}$  M) photopotential and photocurrent was found to increase to maximum value and then decrease in electrical output because fewer reductant molecule, were available for electron donation to photosensitizer (Dye) molecule. Higher concentration of reductant again resulted in a decrease in electrical output, because the large numbers of reductant molecules hinder the dye molecule from reaching electrode in the desired time limit. Thus the higher concentrations of reductant also result in decrease in power output of cell.

### 3.2. Effect of variation of pH

The electrical output of the photogalvanic cell was affected by the variation of pH on the system was found to be quite sensitive to pH of the solution. The photopotential and photocurrent is increased with increase pH value (in alkaline range) of the cell. At pH 10.69 a maxima was obtained, further increase in pH there was decreased photopotential and photocurrent.

It was observed that the performance of the cell is poor in relatively acidic medium. It may be due to proton attachment in dye and reductant leading poor electron donating power of dye and reductant to platinum electrode. In alkaline medium the anion formation of dye and reductant (Ascorbic acid) enhances electron donating power of dye and reductant. At high pH OH<sup>-</sup> ions (comes from NaOH) may combine with cationic reductant (Ascorbic acid) inhibiting regeneration of reductant in original form leading to poor performance of the cell (Fig. 4). The results showing the effect of pH are summarized in Table 2.

### 3.3. Effect of diffusion length and electrode area

Effect of variation of diffusion length on the current parameters of the cell ( $i_{\max}$ ,  $i_{\text{eq}}$ ) initial rate of generation of photocurrent are studied using H-shaped cell of different diameters.  $i_{\max}$  found to increase with diffusion length. It was observed that in the first few minutes of illumination there is sharp increase in the photocurrent. The conductivity of electroactive species depends on its population between electrodes. As diffusion length increased, the volume of dye solution and intern population of dye molecule (Biebrich scarlet) increased leading higher  $i_{\max}$  the electroactive nature of dye/dye<sup>-</sup> is provide by the fact that  $i_{\max}$  increase with diffusion length [32]. There for it may be concluded that the main electro active species are the leuco or semi form of dye<sup>-</sup> and the dye in the illumination and the dark chamber respectively. The reductant its oxidation products act only as electron carriers in the path the result are summarized in Table 3.

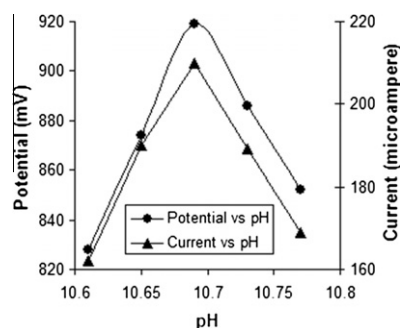


Fig. 4. Effect of pH.

Table 2  
Effect of pH.

pH	Photopotential (mV)	Photocurrent ( $\mu$ A)
10.61	828	162
10.65	874	190
10.69	919	210
10.73	886	189
10.77	852	169

<sup>a</sup>(Tween 60) =  $1.20 \times 10^{-3}$  M, <sup>b</sup>(Biebrich scarlet) =  $4.8 \times 10^{-5}$  M, <sup>c</sup>(Ascorbic acid) =  $2.08 \times 10^{-3}$  M, <sup>d</sup>Light intensity =  $10.4 \text{ mW cm}^{-2}$ , <sup>e</sup>Temp. = 298 K.

Table 3  
Effect of diffusion length.

Diffusion length $D_L$ (mm)	Maximum photocurrent $i_{\max}$ ( $\mu$ A)	Rate of initial generation of current ( $\mu\text{A min}^{-1}$ )
50.0	191.0	7.9583
55.0	212.0	8.8333
60.0	235.0	9.7916
65.0	258.0	10.7500
70.0	280.0	11.6667

<sup>a</sup>(Tween 60) =  $1.20 \times 10^{-3}$  M, <sup>b</sup>(Biebrich scarlet) =  $4.8 \times 10^{-5}$  M, <sup>c</sup>(Ascorbic acid) =  $2.08 \times 10^{-3}$  M, <sup>d</sup>Light intensity =  $10.4 \text{ mW cm}^{-2}$ , <sup>e</sup>Temp. = 298 K, <sup>f</sup>pH = 10.69.

The effect of variation of electrode area on the current parameters of the cell was studied. Experimentally, it was observed that with increase electrode area the value of maximum photocurrent ( $i_{\max}$ ) was found to increase. Maximum output obtained at area  $1 \times 1 \text{ cm}^2$ . For electrode area larger than this the cell parameters were found decreasing with increase in electrode area (Table 4). For the observed effect of electrode area, the better cell parameters were found for small electrodes owing to relatively less hinderence to diffusion of ions as this cell is based on ion diffusion mechanism.

### 3.4. Current–voltage ( $i$ – $V$ ) characteristics

The regular rise in photopotential has been observed as a result of increase in number of excited and electron donating dye molecules during charging of the cell by illumination. The  $i$ – $V$  characteristic shows inversely proportional relation between current and potential. Open circuit voltage;  $V_{\text{oc}}$  (1072 mV) and short circuit current;  $i_{\text{sc}}$  (210  $\mu$ A) of the photogalvanic cell were measured under the continuous illumination of light, with the help of digital pH meter (keeping the circuit open) and a microammeter (keeping the circuit closed), respectively. The external parameters (photopotential and photocurrent) of the photogalvanic cell in between this two extreme values ( $V_{\text{pp}}$  and  $i_{\text{pp}}$ ) were recorded with the help of a carbon pot (log407 K) connected in the circuit of microammeter,

**Table 4**  
Effect of electrode area.

Electrode area (cm <sup>2</sup> )	Maximum photocurrent $i_{\max}$ (μA)	Equilibrium photocurrent $i_{eq}$ (μA)
0.25	194.0	182.0
0.64	219.0	194.0
1.00	235.0	210.0
1.21	249.0	218.0
1.96	292.0	240.0

<sup>a</sup>(Tween 60) =  $1.20 \times 10^{-3}$  M, <sup>b</sup>(Biebrich scarlet) =  $4.8 \times 10^{-5}$  M, <sup>c</sup>(Ascorbic acid) =  $2.08 \times 10^{-3}$  M, <sup>d</sup>Light intensity =  $10.4 \text{ mW cm}^{-2}$ , <sup>e</sup>Temp. = 298 K, <sup>f</sup>pH = 10.69.

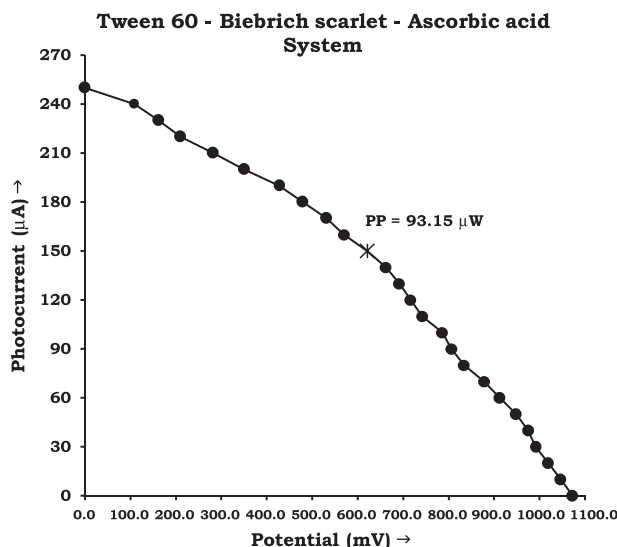


Fig. 5. Current – potential ( $i$ – $V$ ) curve of the cell.

through which an external load applied on it. The power of the cell is taken as a product of current and corresponding potential. When potential is highest (open circuit condition), power is zero due to zero current in the circuit. Similarly, when current is highest (closed circuit condition), power is nearly zero due to nearly zero potential. Therefore, there is maximum power of the cell corresponding to nearly middle values of short circuit current. The  $i$ – $V$  curve of the cell containing Tween 60 – Biebrich scarlet – Ascorbic acid system is shown in Fig. 5. A point in  $i$ – $V$  curve, called power point (pp), was determined where the product of current and potential was maximum and shown as  $V_{pp}$  and  $i_{pp}$ . The fill-factor was calculated as 0.41 using equation:

$$\text{Fill-factor (ff)} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad (\text{xv})$$

### 3.5. Storage capacity (performance) and conversion efficiency of the cell

During study of cell performance in absence of illumination, the power decreases with time (Fig. 6). The cell performance was determined in term 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 can be used in dark for 75.0 min. with Tween 60 – Biebrich scarlet – Ascorbic acid system in photogalvanic cell. The conversion efficiency of the cell was determined as 0.8967% using the relationship

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{A \times 10.4 \text{ mW cm}^{-2}} \times 100\% \quad (\text{xvi})$$

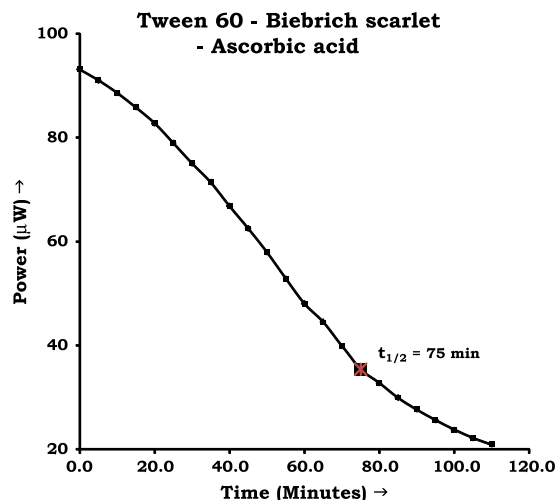


Fig. 6. Time – power curve of the cell.

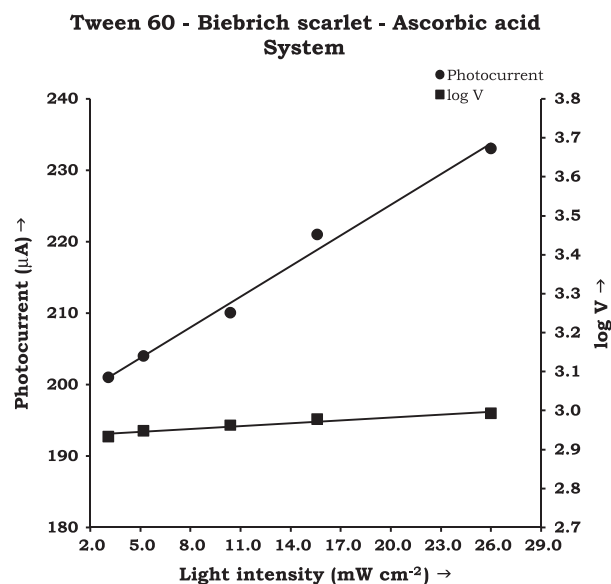


Fig. 7. Variation of photocurrent and  $\log V$  with light intensity.

### 3.6. Effect of variation of light intensity

The intensity of light is also affects the electrical output of the cell. This effect was observed by using solarimeter. It was observed that photocurrent showed a linear increasing behavior with the increase in light intensity whereas photopotential increase in logarithmic manner (Fig. 7). Increase light intensity increases the number of photons per unit area (incident power) striking the dye molecules around the platinum electrode and therefore, an increase in the electrical output. At lower intensity, number of photons may be few in comparison to dye molecule leading to few number of dye molecule for electron donating to platinum electrode. As light intensity increases the number of dye molecules for electron donation to platinum electrode increases and hence electrical parameters increases.

## 4. Conclusions

Solar energy has enormous potential as a clean abundant and economical energy source, but cannot be employed as such; it



must be captured and converted into useful forms of energy. Since solar energy is diffuse and intermittent, conversion should involve concentration and storage. The solar energy conversion efficiency of photogalvanic cell is the essential electrical parameter with respect to maximum energy production, storage and minimum cost. Significant advancement in basic science however, is needed for this technology to attain its full potential. The photopotential, photocurrent and maximum power obtained in present system with anew dye as photosensitizer are 919 mV, 210  $\mu$ A and 192.29  $\mu$ W, these are higher than reported by Dube and Sharma [33,34], with use of Azur dyes. They reported these values as 375 and 340 mV, 70 and 60  $\mu$ A and 18.75  $\mu$ W, respectively. The present work has given an impetus to explore the more suitable selection of surfactant, reductant and photosensitizer for solar energy conversion and storage and to reach maximum energy efficiency.

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