

Research article

Study of Storage Performance in Photogalvanic Solar Cell composed of Photosensitizer – Sufactant -Reductant system

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Abstract

Photogalvanic effect is studied in photogalvanic cell system containing crystal violet as a photosensitizer, EDTA as a reductant in photogalvanic cell system. Various electrical parameters of the cell were observed. Current-voltage characteristics, Fill factor & conversion efficiency of cell is observed, effects of variation of EDTA, DSS and crystal violet concentration, pH, light intensity, electrode area, temperature and diffusion length of the cell were observed. Storage capacity of the cell is obtained as 140 minutes in dark. The photopotential and photocurrent generated by this system were 835.0 mV and 110.0 μ A respectively. A tentative mechanism of the photogalvanic cell reaction was also proposed. Spectral properties of cell solution were also studied with the help of spectrophotometer. **Copyright © AJBCPS, all rights reserved.**

Keywords: Solar cell, Photogalvanic cell, Photopotential, Photocurrent, fill factor, efficiency and half time.

Introduction

The use of energy is important for human society for handling problems in the environment. Developed societies use energy resources for agriculture, transportation and the trend has increased since the industrial

revolution. This has brought a number of serious problems to global environment such as global warming. In the past century, it has been seen that the consumption of non-renewable sources of energy has caused more environmental damage than any other human activity and electricity generated from fossil fuels such as coal and crude oil has led to high concentrations of harmful gases in the atmosphere. This in turn led to many problems such as ozone depletion and global warming. Vehicular pollution has also been a major problem. Therefore, alternative sources of energy have become very important and relevant to today's world. These sources, such as the sun and wind, can never be exhausted and therefore are called renewable. They cause less emission and are available locally. Their use can, to a large extent, reduce chemical, radioactive and thermal pollution. They stand out as a viable source of clean and limitless energy.

Most of the renewable sources of energy are fairly non-polluting and considered clean though biomass, a renewable source, is a major polluter indoors. Solar energy is the most readily and freely available source of energy. It is also the most important of the non-conventional sources of energy because it is non-polluting and, therefore, helps in lessening the greenhouse effect. A new hypothesis is thus developed to introduce solar energy conversion into electrical energy by studying photogalvanic effect in photogalvanic solar cell based on photochemical reaction which gives rise to high energy products on excitation by quanta or short energy packets.

The photogalvanic effect was first of all recognized by Rideal and Williams [1] and it was systematically studied by Rabinowitch [2-3]. Later on studies in photogalvanic cell systems with various sensitizers for solar energy conversion and storage reported by Potter and Thaller [4], John [5] Hamdi and Aliwi [6] Pokhrel and Nagaraja [7]. Markovet et. al [8-9], Bayer et. al [10], John and Ramraj [11], Ameta et. al [12], Madhwani et. al [13] Kumari et. al [14], Rohtagi-Mukherji et al[15], Folcher and Paris [16], Alfredo and Georgina[17], Pan et al. [18], Dube et. al [19-20], Lal [21], Grochen et al. [22] and Baurle and Kroiner [23], recently developed some photogalvanic systems for solar energy conversion and storage. They have used different micellar species, photosensitizers, and reductants in photogalvanic cells. In this field Genwa and Co-workers reported some new photogalvanic cells in view of electrical parameters and solar energy conversion and storage [24-33]. In the present work, H-shape cell was used in study of Photogalvanic effect and energy efficiency in Photogalvanic cell composed of Crystal violet as a photosensitizer in DSS –EDTA system and studies electrical parameters and energy efficiency in photogalvanic cell.

Material and Methods

In the photogalvanic cell system Crystal violet (Ranbaxy), EDTA (Ranbaxy), Dioctyl sulphosuccinate sodium salt (Loba), Sodium hydroxide (Ranbaxy) and Oxalic acid were used (Table-1). The stock solutions of EDTA ($2.24 \times 10^{-3} \text{M}$), Crystal violet ($4.4 \times 10^{-4} \text{M}$), DSS ($1.76 \times 10^{-3} \text{M}$) and sodium hydroxide (1M) were prepared in doubly distilled water and kept in amber coloured containers to protect them from sun light. A mixture of solutions of dye (Crystal violet), reductant (EDTA), surfactant (Dioctyle sulphosuccinate sodium salt) and sodium hydroxide taken in a blackened H-Shaped (Fig. 1) glass container to keep the total volume of reaction mixture always 25.0 ml. A platinum foil electrode ($1.2 \times 1.2 \text{ cm}^2$) was immersed in to one limb of H-shaped glass container and Saturated calomel electrode (SCE) was immersed in another limb. The whole system was first placed in dark. When stable potential (mV) is obtained in dark, it was measured. Then another limb

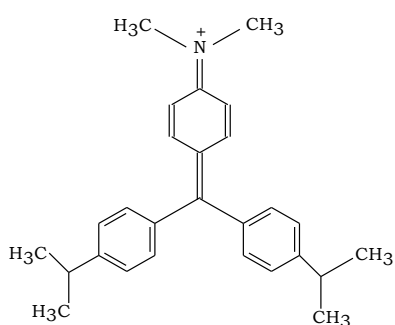
containing the SCE was kept in dark and limb containing platinum foil electrode was exposed to a tungsten lamp of different wattage. A water filter was placed between the light source and cell to cut-off infra-red radiations.

Absorption spectra of dye solution have also been taken with the help of U-Vis. Spectrophotometer (Systronics 108). The pH of the system was adjusted by adding the desired volume of standard NaOH solution. pH of the reactive system was measured by a digital pH meter (Systronics model 135). Photopotential and photocurrent generated by this system were measured by a digital pH meter and microammeter (OSAW 1632/A), respectively. Current-voltage (i-V) characteristics of the cell were studied using an external load resistance (log 470 K) in microammeter circuit.

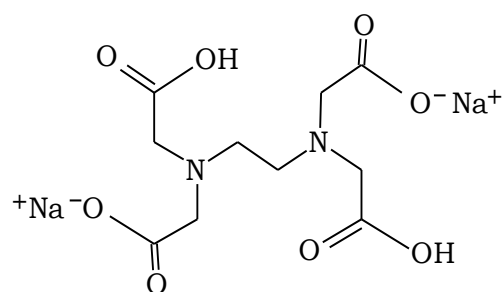
Table-1: Chemical and physical properties of compounds used:

| S. No. | Name of Chemical | Molecular Formula | Molar Mass | Solubility | M.P. | Colour | CAS No. |
|--------|------------------------------------|---|--|---------------|-----------|------------------------------|-----------|
| 1. | Crystal Violet | C ₂₅ N ₃ H ₃₀ Cl | 407.97 g/mol | Water soluble | 205 °C, | Blue-violet | 548-62-9 |
| 2. | Ethylene diamine tetra acetic acid | C ₁₀ H ₁₆ N ₂ O ₈ | 292.24 g/mol | Water soluble | 237 °C | White powder | 6381-92-6 |
| 3. | Dioctyle sulpho succinate | C ₂₀ H ₃₇ NaO ₇ S | 444.56 g/mol | Water soluble | 153–157°C | White powder | 577-11-7 |
| 4. | Sodium Hydroxide | NaOH | 39.997 g/mol | Water soluble | 318 °C | White pallets | 1310-73-2 |
| 5. | Oxalic acid (dihydrated) | (COOH) ₂ .2H ₂ O | 126.07 g mol ⁻¹ (dihydrate) | Water sluble | 52.5-53.5 | Colourless crystalline solid | 6153-56-6 |

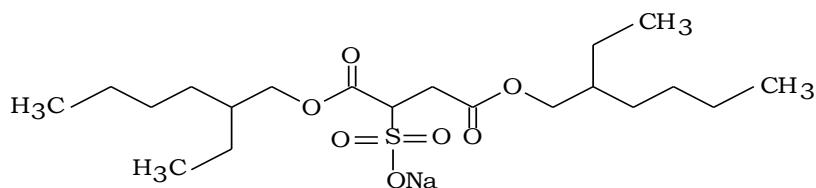
Structure of compounds used:



Crystal Violet



EDTA



DSS Sodium Salt

Results and discussion

A. Study of absorption property of dye

The spectral properties of photosensitizer (Crystal Violet) studied with the help of Double Beam UV-VIS Spectrophotometer (Systronics Model no. 106). It was observed that the photosensitizer shows absorption peak (λ_{max}) in visible region with maximum at 594 nm. Absorption spectrum of photosensitizes after adding known concentration of surfactant solution spectra of absorption shift toward longer wavelength is called Red Shift due to Change of concentration of DSS. The concentration of crystal violet and DSS solution for the experiment were kept at 4.4×10^{-4} M and 1.76×10^{-3} M respectively. The changes in the spectra can shown in Fig. 2.

B. Current-potential (*i-V*) characteristics and Fill factor of the cell

The open circuit voltage (V_{oc}) and short circuit current (i_{sc}) of the photogalvanic cell were measured under the continuous illumination of light, with the help of a digital pH meter (keeping the circuit open) and a microammeter (keeping the circuit closed), respectively. The electrical parameters (photopotential and photocurrent) of photogalvanic cell in between these two extreme values (V_{pp} and i_{pp}) were recorded with the help of a carbon pot (log 470 K) connected in the circuit of microammeter, through which an external load applied on it (Fig. 3). It was observed that *i-V* curves deviated from standard regular rectangular shape (found in standard condition of 0° C and 1000W/m^2 insolation and in typical condition 25°C and 800W/m^2 insolation for the solar cells). By *i-V* curve a point was determined where product of potential (V_{pp}) and current (i_{pp}) was maximum, called power point (pp). With the help of *i-V* curve, the fill factor of photogalvanic cell was determined as 0.4054, using following formula:-

$$\text{Fill factor (ff)} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad (1)$$

Where V_{pp} , i_{pp} , V_{oc} , i_{sc} are the potential at power point, current at power point, open circuit voltage and short circuit current.

C. Effect of variation of pH

Effect of pH on cell system was observed by using NaOH solution of different concentration. Photogalvanic cell containing Crystal violet-Oxalic acid-DSS system was found quite sensitive to the pH of the solution. The electrical output of photogalvanic cell was affected by the variation in pH of the system. It was noticed that there an increase in the photopotential and photocurrent of this system with increase pH in alkaline range. At pH 12.9 a maximum was obtained and it's shown in Fig. 4. There was a decrease in photopotential and photocurrent with further increase pH of the system.

D. Effect of dye, reductant and surfactant concentration

The photogalvanic effect is observed by variation of the concentration of Crystal violet. Photopotential and photocurrent dependence on the concentration of dye (C V) was studied. It was observed that the lower concentration of dye shows fall into cells electrical output because there should be low availability of dye molecules for excitation and consecutive donation of the electrons to the platinum electrode. Similarly at the higher concentration of dye fall in electrical output observed because major portion of light is absorbed by the dye molecules present in path so in the vicinity of platinum electrode the desired light intensity will not obtained by dye molecules.

Effect of reductant concentration studied using different concentration of Oxalic acid. It was observed that with the increase in concentration of the reductant (Oxalic acid), the photopotential and photocurrent were found to an increase till it reaches a maximum. A decrease in the electrical output of the cell on further increase in reductant concentration was recorded. Lower concentration of reducing agent shows fall in electrical output of the cell because fewer molecules of reducing agent will be available for electron donation to reduce the dye molecules. Similarly the large concentration shows fall in to electrical output of the cell because in the desired time the large number of reductant molecules hinders the dye molecules reaching towards the platinum electrode.

Various concentration of surfactant used to observe the effect of Dioctyl Sulphosuccinate concentration. It was obtained that with increasing surfactant concentration the photopotential and photocurrent of the cell were increased, attains a maximum at a particular surfactant concentration and decreases on further increase in surfactant concentration. Results of these parameters are shown in Fig. 5.

E. Effects of variation of Diffusion Length

The effects of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell were observed using H-shaped glass containers (Fig. 6) of different dimensions. It was observed that maximum photocurrent (i_{max}) and rate of initial generation of photocurrent increases with diffusion length. It is observed that the dye itself is the main electroactive species and the leuco or semi reduced form of dyes at the dark and illuminated compartments of the photogalvanic cell respectively. However the reductant and its oxidized products act only as electron carriers in the path.

F. Effect of Light Intensity

The electrical output of photogalvanic cell obtained by this system was studied using light source of different intensities (watts). It was found that photopotential increased with increasing light intensity in a logarithmic manner whereas, photocurrent showed a linear increasing behaviour with the increase in light intensity and results are shown in Fig. 7.

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

The storage capacity of the photogalvanic cell system containing Crystal violet was determined by applying the desired external load with keeping the cell at the power point stage in dark and noted down the time required in fall of power output to its half value. Storage capacity of the photogalvanic cell system is denoted by $t_{1/2}$, is the measure of performance of the cell. It was observed that cell can be used in the dark for 140 minutes. With the help of electrical output (potential and current) at power point and the incident power of radiations the conversion efficiency of photogalvanic cell was calculated as 0.36 % by using the formula:

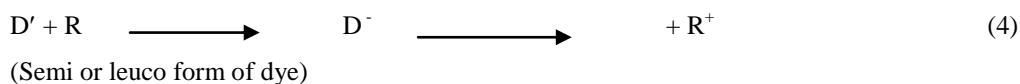
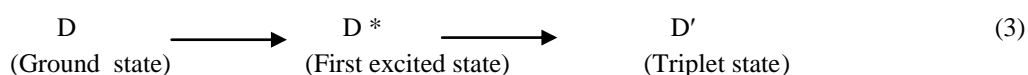
$$\text{Conversion Efficiency } (\eta) = \frac{V_{pp} \times i_{pp}}{10.4 \text{ mW cm}^{-2}} \times 100\% \quad (2)$$

Where V_{pp} , i_{pp} and A are photopotential at power point, photocurrent at power point and electrode area, respectively and it is presented in the form of graph in Fig. 8.

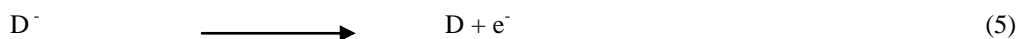
Mechanism of Reaction

Chemically, the reactive species is triplet state of dye specially, in the presence of electron donating substances the dye is excited by light and rapidly changed into reduced (colorless) form. The dye acts as a reducing agent and will be donating electrons to other substances and being returned to its oxidized state. On the basis of these observations a mechanism is suggested for the generation of electrical output in photogalvanic cell as follows

Illuminated Chamber

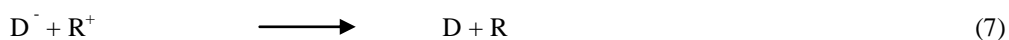
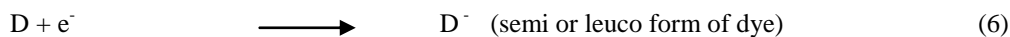


At platinum electrode:



Dark Chamber

At SCE:



Where D , D^* , D^- , R and R^+ represents the dye (C.V.), excited form of dye, reduced form of dye, reductant and oxidized form of reductant, respectively and schematic diagram is shown in Fig. 9.

Conclusion

The photogalvanic conversion of solar energy has attracted attention of scientists towards solar energy conversion and storage. Considering the limited efforts and the time spent so far on the development of photogalvanic cells, the results appear encouraging and efforts are continuously made in this direction to increase conversion efficiency and storage capacity using different photosensitizers. If it is possible to make an improvements developed methods by many researchers they are likely to help in the task of putting solar energy to the service of mankind. On the basis of studies and obtained results in developed photogalvanic cell it can be concluded that Crystal Violet system is the efficient system and can be use in photogalvanic cell for solar energy conversion and storage. It has been observed that the anionic surfactants and reductants have not only enhanced the conversion efficiency but also the storage capacity of the cell. Photogalvanic cells have the advantages of having in-built storage capacity. Thus, photogalvanic cells showed good prospects of becoming commercially viable.

References

- [1] E. K. Rideal and E. G. Williams, The action of light on the ferrous iodine iodide Equilibrium, *J. Chemical Soci. Trans.*, 127,1925, 258–269.
- [2] E. Rabinowitch, The Photogalvanic Effect I: The Photochemical Properties of the Thionine-Iron System, *J. Chemical Phy.*, 8,1940, 551–559.
- [3] E. Rabinowitch, The Photogalvanic Effect II: The Photogalvanic Properties of Thionine-Iron System, *J. Chemical Phy.*, 8,1940, 560–566.
- [4] A.E. Potter and L.H. Thaller, Efficiency of some iron-thionine photogalvanic cells, *Solar Energy*, 3,1959, 1-7.
- [5] W. John Albery Development of photogalvanic cells for solar energy conservation, *Acc. Chem. Res.*, 15, 5; 1982,142–148.
- [6] S. T. Hamdi and S. M. Aliwi, The photogalvanic effect of Fe (II)-beta-diketonate/thionine systems in aqueous acetonitrile, *Monatshefte fuer Chemie*, 127, 1996, 339-346.
- [7] S. Pokhrel and K. S. Nagaraja, Photogalvanic behavior of [Cr2O2S2(1-Pipdte)2(H2O)2] in aqueous DMF, *Solar Energy Materials and Solar Cells*, 93, 2009, 244-248.
- [8] P. Markov, M. Novkirishka and K. Aljanapy, Photopotential and photocurrent induced by an aqueous solution of aliphatic alcohols, *J. Photochem. Photobiol. A: Chem*, 96, 1996, 161-165.
- [9] P. Markov and M. Novkirishka, On the photogalvanic properties of alkylpyridinium salts in Solution, *Electrochemical Acta*, 36, 1991, 1287-1291.
- [10] L. S. Bayer, I. Erogle and L. Turker, Photogalvanic effect in aqueous methylene blue Ni mesh system: conversion of light in to electricity, *Int. J. of Energy Research*, 25, 2001, 207-222.
- [11] S. A. John and R. J. Ramraj, Micro environment effect on electrochemical and photoelectrochemical properties of thionine loaded Nafion film, *J. Electroanal. Chem*, 561, 2004, 119-126,
- [12] S.C. Ameta, P. B. Punjabi, J. Vardia, S. Madhwani and S. Chaudhary, Use of bromophenol red–EDTA system for generation of electricity in a photogalvanic cell, *J. Power Sources*, 159,2006, 747-751.
- [13] S. Madhwani, J. Vardia, P. B. Punjabi and V. K. Sharma, Use of fuchsine basic:EDTA system in photogalvanic cell for solar energy conversion, *Proceedin of the Institution of Mechanical Engineers, Part A: J. power and Energy*, 221, 2007, 33- 39.
- [14] M. Kumari, R. B Pachwaria and R. C. Meena, Studied of dye sensitization for solar energy conversion in to electrical energy in cango Red- EDTA system, *Energy Sources Part A*, 32,2009,1081-1088.
- [15] K. K. Rohatgi-Mukherji, M. Roy, and B. B. Bhowmik, Photovoltage Generation of the Phenosafranine Dye-EDTA Sandwich Cell, *Solar Energy*, 31, 1983, 417–418.
- [16] G. Folcher and J. Paris, “Photogalvanic Cell”, Paris, J. US Patent, 4391881, 1983.
- [17] O. Alfredo, P. Georgina, and P. J. Sebasteian, Electron Transfer via Organic Dye for Solar Energy Conversion, *Solar Energy Material & Solar Cells*, 59, 1990, 137–143.
- [18] R. L. Pan, R. Bhardwas, and E. L. Gross, “Photochemical Energy Conversion by a Thiazine Photosynthetic Photoelectrochemical Cell”, *J. Chem. Tech. and Biotech. Chemtech.*, 33, 1993, 39–48.
- [19] S. Dube, S. L. Sharma, and S. C. Ameta, “Photogalvanic Effect in Azur B -NTA System”, *Energy Conversion & Manag.*, 38, 1997, 101–106.
- [20] S. Dube, “Simultaneous Use of Two Reductants in a Photogalvanic Cell for Solar Energy Conversion and Storage”, *Int. J. Energy Res.*, 17, 2007, 311–314
- [21] Chhagan Lal, “Use of Mixed Dyes in a Photogalvanic Cell for Solar Energy Conversion and Storage :

- EDTA – Thionine – Azur B System”, J. Power Sou., 164, 2007, 926–930.
- [22] E. J. J. Grochen, M. S. De Groat, R. De Ruitter, and N. De, J. Phys. Chem., 88,1989, 1449–1454
- [23] S. A. Baeurle and J. Kroiner, “Modeling Effective Interactions of Micellar Aggregates of Ionic Surfactants with the Gauss-Core Potential”, J. Mathematical Chem., 36, 2004, 409–421.
- [24] K.R. Genwa and A. Chouhan, Studies of effect of heterocyclic dye in photogalvanic cell for solar energy conversion and storage NaLS -ascorbic System, J. Chem. Sci., 116, 2004, 339-345.
- [25] K.R. Genwa and A. Chouhan, Role of heterocyclic dye (Azur A) as a photosensitizer in photogalvanic cell for solar energy conversion and storage, NaLS-ascorbic acid system, Solar Energy, 80, 2006, 1213-1219.
- [26] K.R. Genwa and A. Sonel, An Approach to Solar energy conversion and storage with Malachite Green-Aribnose-NaLS system, J. Ind. Council Chem., 24, 2007, 78-81.
- [27] K.R. Genwa and A. Kumar, Studies in Nile blue-NaLS System for solar energy conversion and Management, photogalvanic performance and Conversion Efficiency, J. Ind. Council.Chem., 26, 2009 181-186.
- [28] K.R. Genwa, A. Kumar and A. Sonel, Photogalvanic solar cell conversion, study with Photosensitizers Toludine Blue and Malachite Green in Presence of NaLS, Appl.Energy, 86, 2009, 1431-1436.
- [29] K.R. Genwa, N.C. Khatri, Comparative Study of Photosensitising dyes in Photogalvanic cells for solar energy conversion and storage: Brij-35- DTPA system, Energy & Fuel , 23, 2009, 1024-1031.
- [30] K.R. Genwa and A. Chouhan; Study of Electrical parameters and Energy Efficiency in Photogalvanic cell Containing Erythrosine as a Photosensitizer in Benzethonium Chloride EDTA System, Energy Sci. and Technol.; 2, 2011, 18-24.
- [31] K..R.Genwa and A.Kumar; Dye Sensitized Photogalvanic Solar Cells: Studies in a Methyl Green-NaLS system in View of Energy Conversion, Energy Sources Part A, 34, 2012, 1261-1270.
- [32] K. R. Genwa and C.P.Sagar, Energy efficiency, solar energy conversion and storage in photogalvanic cell, Energy conversion and Management, 66, 2013, 121-126.
- [33] K.R. genwa and Keval Singh, Optimum Efficiency of Photogalvanic Cell for Solar Energy Conversion: Lissamine Green B-Ascorbic Acid-NaLS System; Smart Grid and Renewable Energy, 4, 2013, 306-311.

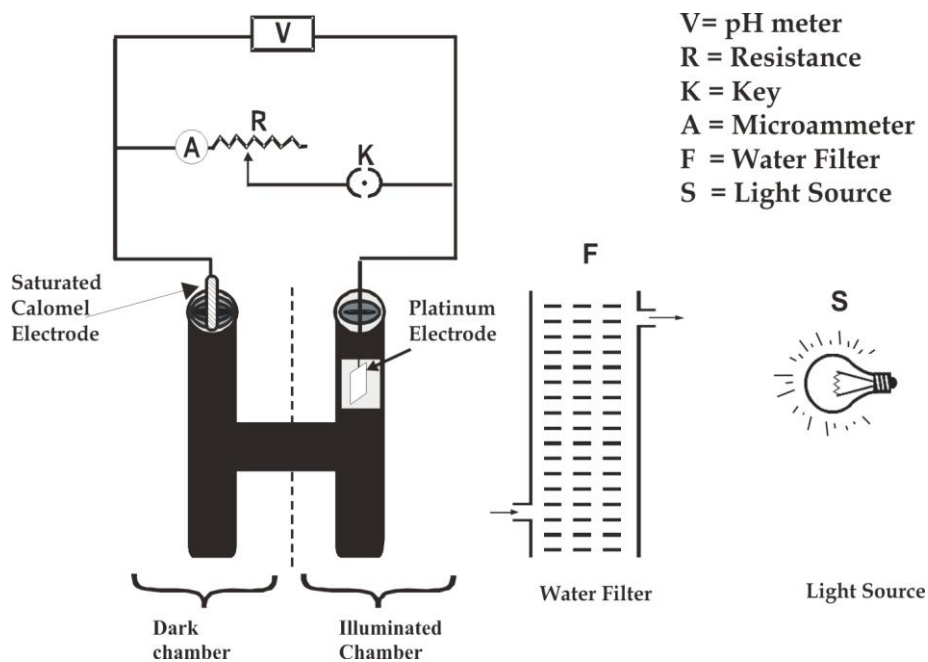


Fig. 1: Photogalvanic cell set-up

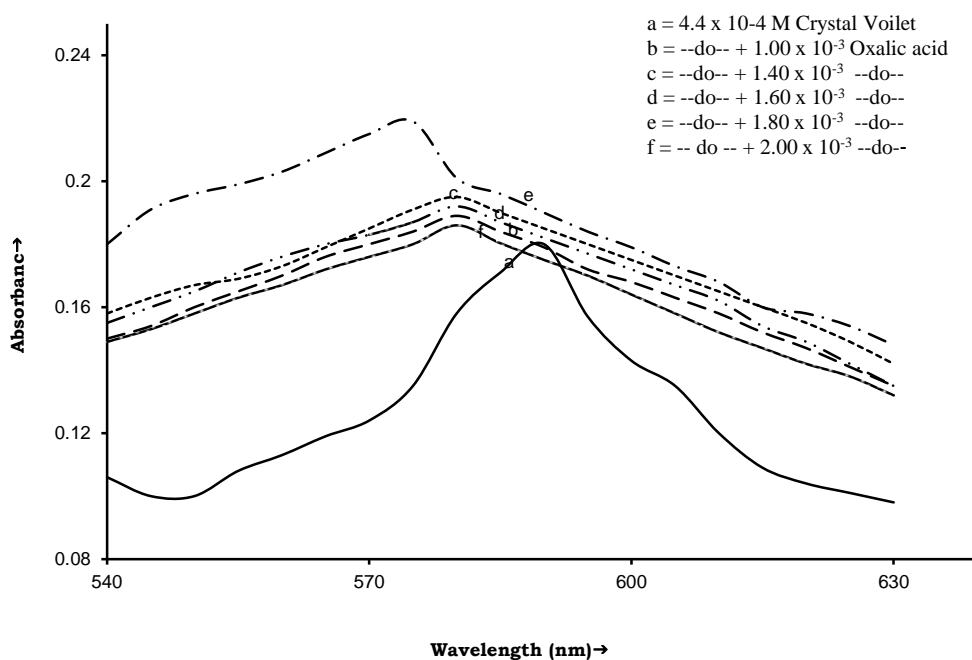


Fig. 2: Adsorption spectra

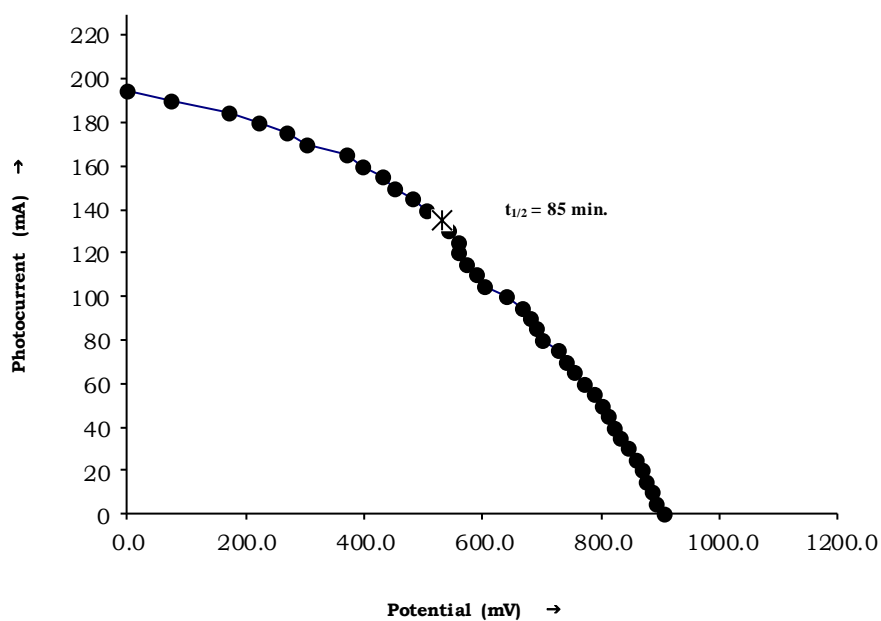


Fig. 3: Current-Voltage curve

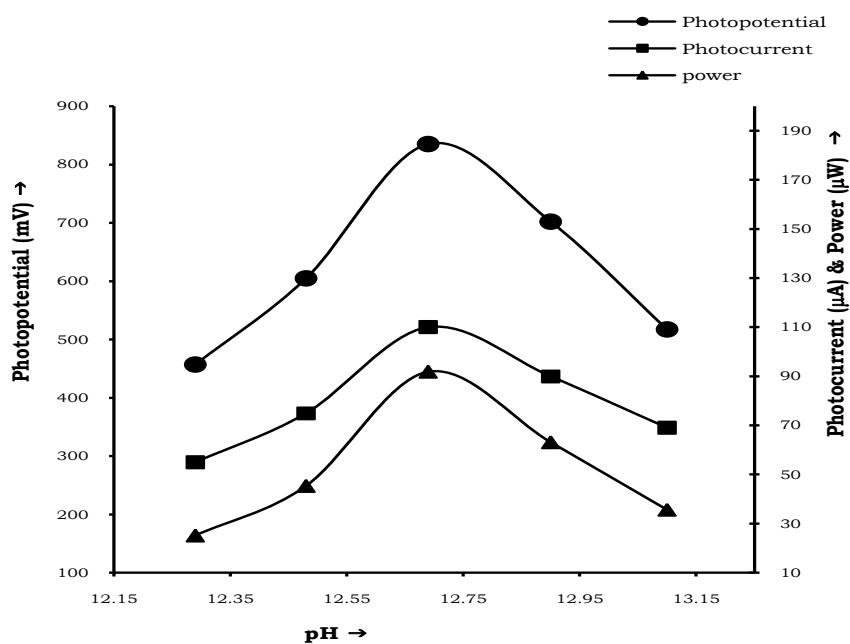


Fig. 4: Effect of pH curve

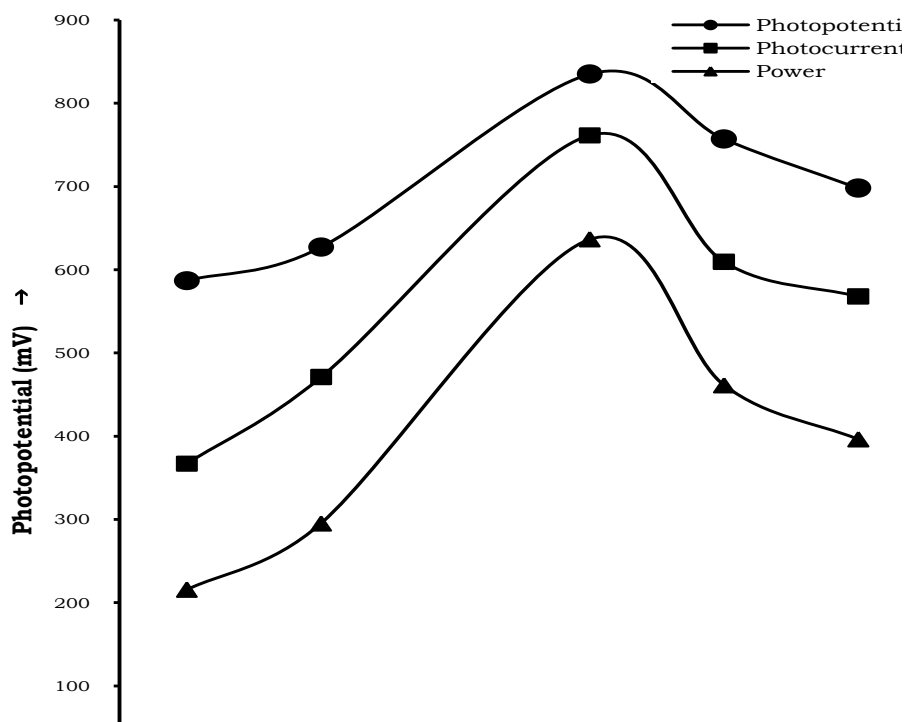


Fig. 5(a): Effect of concentration of Crystal violet curve

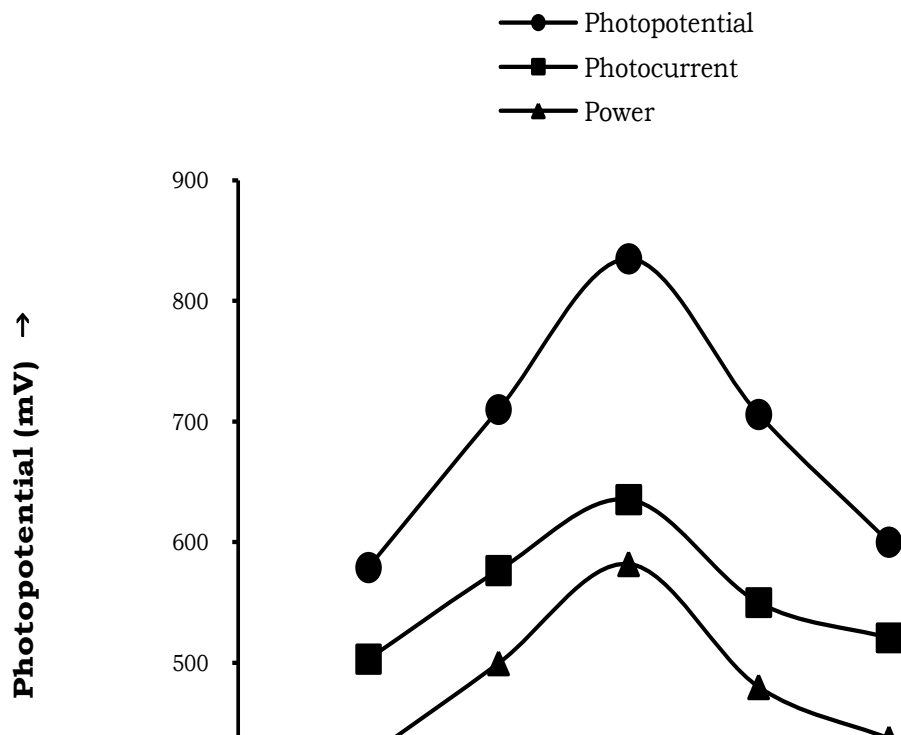


Fig. 5(b): Effect of concentration of EDTA curve

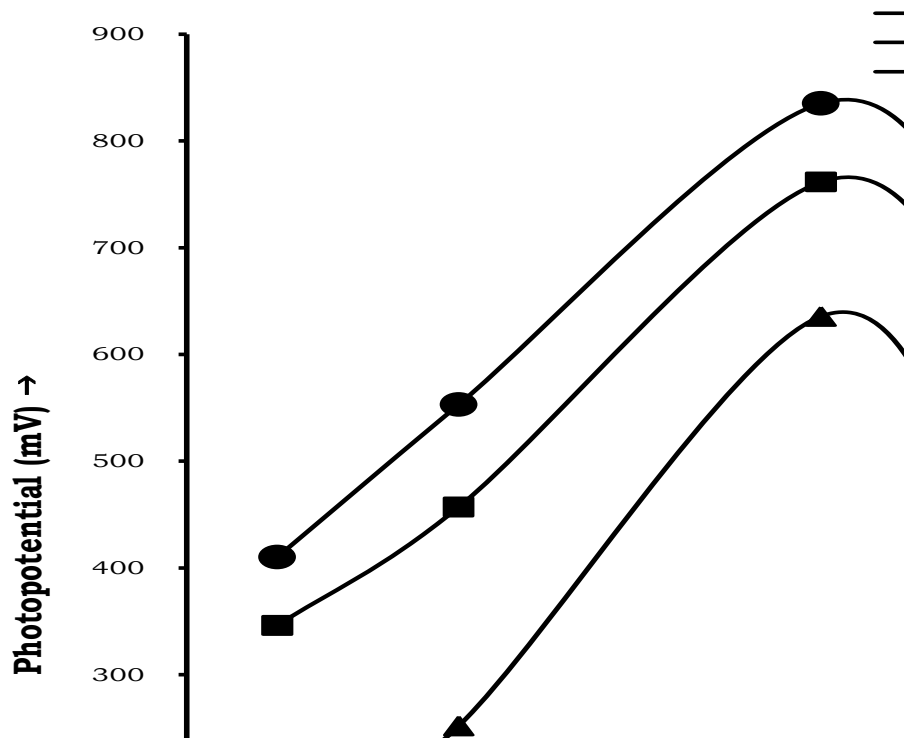


Fig. 5(c): Effect of concentration of DSS sodium salt curve

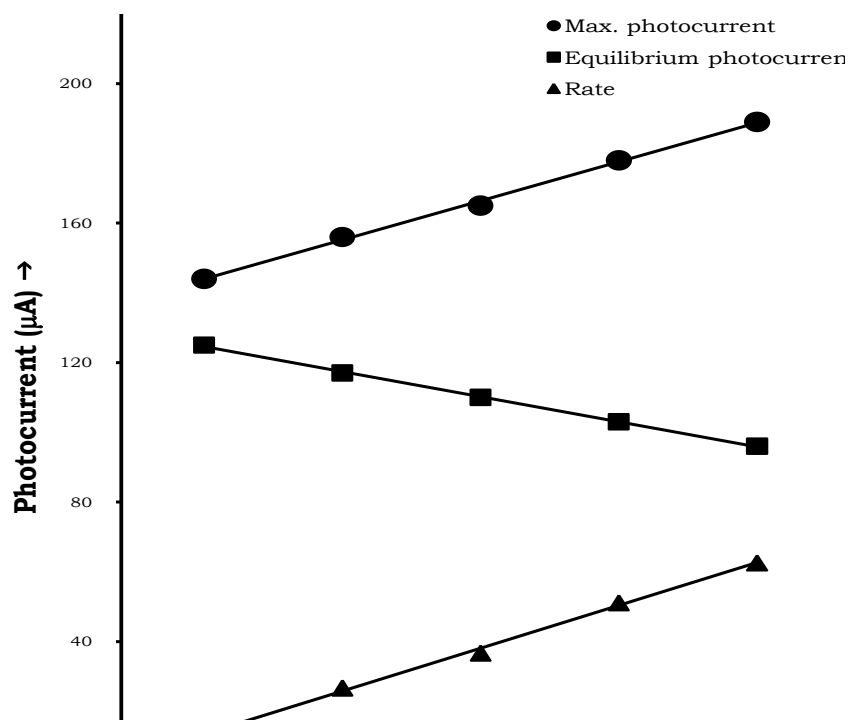


Fig. 6: Effect of diffusion length curve

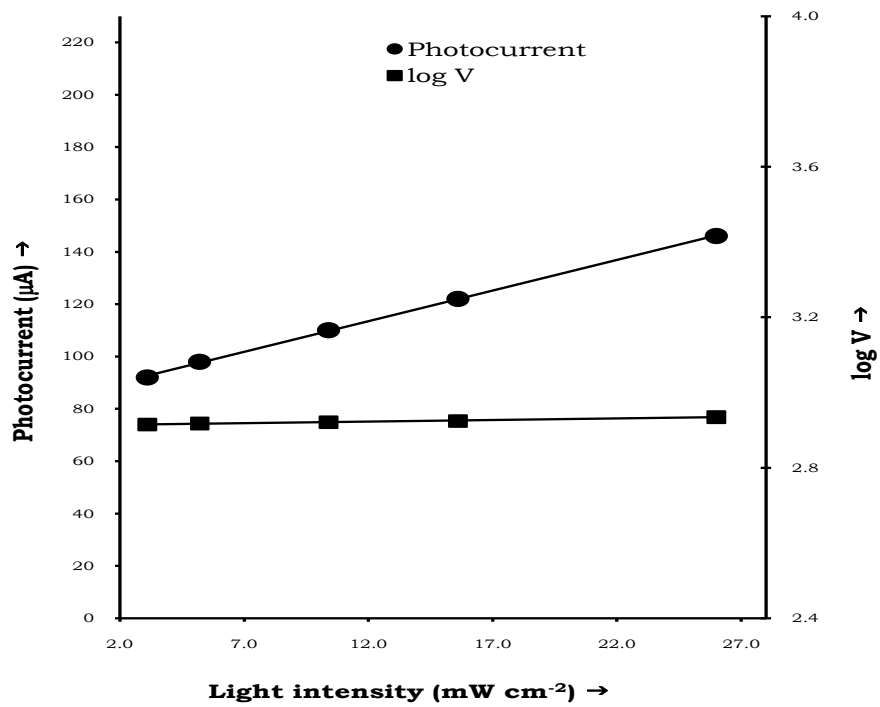


Fig. 7: Light intensity

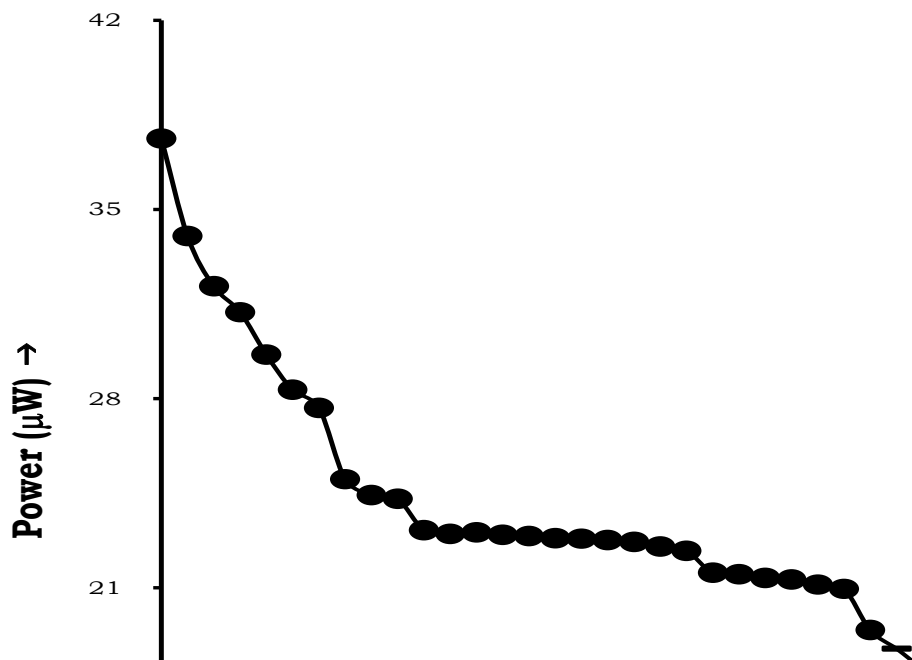


Fig. 8: Performance of the cell

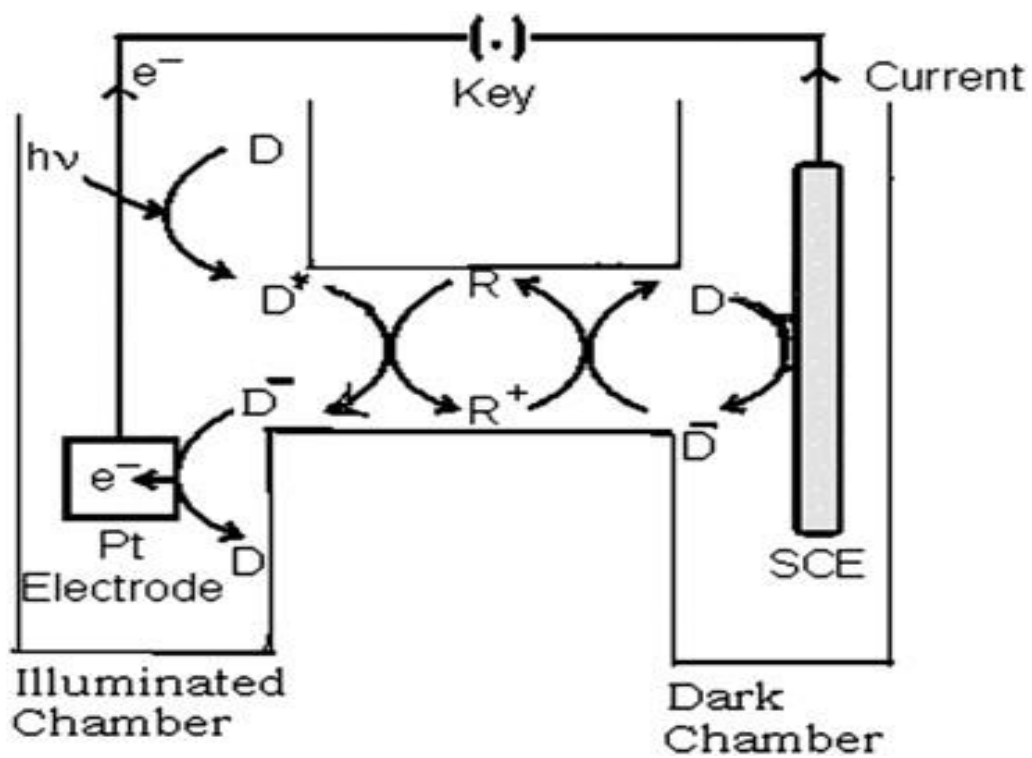


Fig. 9: Mechanism of redox reaction