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Manoj Kumar
Ram Krishna College
Madhubani, Bihar, India

Sonu Ram Shankar
University Department of
Chemistry, Lalit Narayan
Mithila University,
Darbhanga, Bihar, India

Bhavesh Kumar Shandilya
Department of Chemistry
Uma Pandey College, Pusa,
Samastipur, Bihar, India

Kewal Singh
Department of Chemistry
S. G. N. Khalsa P. G. College
Sri Ganganagar, Rajasthan,
India

Corresponding Author:
Bhavesh Kumar Shandilya
Department of Chemistry
Uma Pandey College, Pusa,
Samastipur, Bihar, India

Comparative evaluation of bromocresol green and naphthol blue black based photogalvanic cells for solar energy conversion and storage

Manoj Kumar, Sonu Ram Shankar, Bhavesh Kumar Shandilya, and Kewal Singh

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Abstract

The comparative performance of photogalvanic cells for solar energy conversion and storage was reported using bromocresol green and naphthol blue black as different photosensitizers, EDTA as a reductant, and Tween 80 as a surfactant in different systems. The maximum photopotentials were 887.0 and 942.0 mV, whereas the photocurrent at equilibrium was 748.0 and 730.0 μ A, respectively. The observed conversion efficiencies for bromocresol green and Naphthol Blue Black with EDTA and Tween 80 were 0.96 and 1.03%, respectively. The fill factors of 0.1509 and 0.1572 were experimentally determined at the power point of the cell. The effects of different parameters on the electrical output of the cell were observed, and the current-voltage (I-V) characteristics of the cell were studied in detail.

Keywords: Bromocresol green, naphthol blue black, photogalvanic effect, conversion efficiency, fill factor, and power at power point

1. Introduction

As natural resources are being exhausted at an ever-increasing pace, when all natural resources of energy are completely exhausted, humans will have no other alternative but to utilize solar energy. It is not only a new, harmless, and low-cost source of energy, but also an inexhaustible source of energy. Although society's electricity needs are largely continuous, photovoltaic solar cells have an intermittent output due to clouds and darkness. In this regard, photogalvanic cells hold great promise for addressing both issues simultaneously by producing electricity via solar energy conversion. Accordingly, renewable energy resources are attracting considerable attention, and solar energy is one of the most promising future energy resources [1]. Developed and developing countries are focusing on the environmental damage caused by conventional energy sources. Renewable energy sources occur in nature and are regenerative or inexhaustible, such as solar, wind, hydropower, geothermal, biomass, tidal, and wave energy. Photogalvanic (PG) cells are photoelectrochemical systems based on the "photogalvanic effect." A PG cell is a device that produces energy through photochemical processes occurring inside the electrolyte solution upon light absorption within a highly absorbing electrolyte, which gives rise to high-energy products upon excitation by a photon. These energy products electrochemically lose photoenergy to generate electricity. These cells are quite different from other solar cells. Different types of dyes as light-absorbing materials, organic/inorganic chemicals as reductants, and anionic/cationic/neutral surfactants as micelles have been exploited for solar energy conversion and storage using PG cell technology. The Naphthol blue black dye has some characteristics that make it a good photosensitizer for use in solar energy harvesting through PG cells. The conversion of solar energy into electrical energy through photogalvanic cells is the most important and desirable route for obtaining electricity. Becquerel [2] was the first to observe the flow of current between unsymmetrically illuminated metal electrodes in sunlight, and the first report on photogalvanics was by Rideal and Williams [3], but it was Systematically investigated by Rabinowitch [4-5]. Later on Kaneko and Yamada [6], Murthy *et al.* [7], Rohatgi Mukherjee *et al.* [8], Folcher and Paris [9], Alfredo *et al.* [10],

Dube *et al.* ^[11], Bayer *et al.* ^[12], Matsumoto *et al.* ^[13] and Shiroishi *et al.* ^[14] have studied some interesting photogalvanic systems. Bisquert *et al.* ^[15] have reviewed the physical-chemical principles of dyesensitized solar cells, whereas Mayer ^[16] has presented the molecular approaches to solar energy conversion. The problems encountered in the development of photogalvanic cells have been discussed previously. Krasnolovets *et al.* ^[17], Madhwani *et al.* ^[18], Gangotri and Bhimwal ^[19], Genwa and Chauhan ^[20], Genwa and Singh ^[21], Rathode *et al.* ^[22-23] have recently developed photogalvanic systems for solar energy conversion and storage. The scientific community has successfully converted solar energy into electrical energy to the desired extent through various processes, but the storage capacity of solar energy is still not up to the mark for use as and when required. Many of them have used different photosensitizers, surfactants, and reductants in photogalvanic cells, but no attention has been paid to the use of this system containing Naphthol blue black dye as an energy material to enhance the electrical output and performance of the photogalvanic cell. Therefore, the present study was undertaken to achieve better performance and commercial viability of photogalvanic cells.

2. Materials and methods

Bromocresol green, Naphthol blue black, EDTA, Tween 80 and NaOH of Loba Chemie were used in the present work. Stock solutions of EDTA, dye, Tween 80, and NaOH (1N) were prepared in double-distilled water (conductivity $3.5 \times 10^{-5} \text{ Sm}^{-1}$) and stored in amber-colored containers to protect them from sunlight. A 25 ml stock solution was placed in an H-type glass tube, which was blackened with black carbon paper to protect it from sunlight. A shiny Pt foil electrode ($1.0 \times 1.0 \text{ cm}^2$) was immersed in one limb of the H-tube, and a Saturated Calomel Electrode (SCE) was immersed in the other limb. The Pt electrode acted as the working electrode, and the Saturated Calomel Electrode (SCE) acted as the counter electrode. The entire system was first placed in the dark until a stable potential was attained, and then the limb containing the Pt electrode was exposed to a 200 W tungsten lamp (Philips). A water filter was used to block the thermal radiation. A digital multimeter (HAOYUE DT830D) was used to measure the photopotential and current generated by the system. The i-V characteristics were studied by applying an external load using a carbon pot (log 470 K) connected in the circuit. The Photogalvanic cell setup and chemical structures are shown in Figures 1 and 2, respectively.

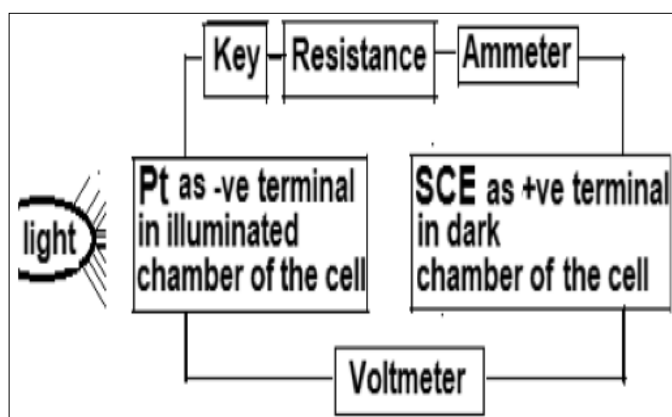


Fig 1: Photogalvanic Cell Set-up

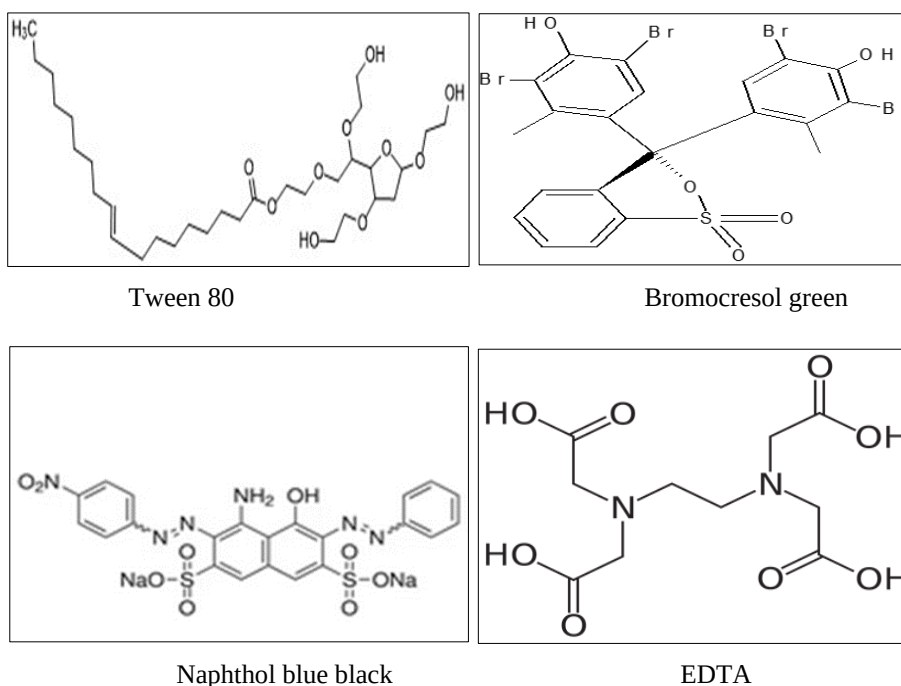


Fig 2: Structures of chemicals

3. Results and Discussion

Effect of variation in dye, reductant, and surfactant concentrations

The photogalvanic effect was studied in a photogalvanic cell containing two dyes, bromocresol green and naphthol blue black, in the presence of the reductant EDTA and surfactant Tween 80. The concentrations of the dyes bromocresol green and naphthol blue black were kept at 2.3×10^{-5} M and 2.2×10^{-5} M, respectively. It was observed that there was an increase in photopotential and photocurrent on increasing the concentration of dye. In the lower concentration range of dyes, there are limited dye molecules to absorb the major portion of the light in the path; therefore, the electrical output is low. In contrast, higher dye concentrations do not permit the desired light intensity to reach the molecules near the electrodes; hence, a corresponding decrease in the power of the cell is observed. EDTA was used as a reductant in the photogalvanic cell. The concentration of the reductant was maintained at 1.8×10^{-3} M and 1.4×10^{-3} M in Bromocresol green-EDTA-Tween-80 and Naphthol blue black-EDTA-Tween-80 systems respectively. With an increase in the concentration of the reductant, the electric output of the photogalvanic cell increased until it reached a maximum value, after which there was a decrease in the photopotential and photocurrent with further increase in the concentration of the reductant. The decrease in power output was also due to the decrease in the concentration of the reductant, which was caused by the lower number of molecules available for electron donation to the dye molecule. On the other hand, the large concentration of reductant again resulted in a decrease in electrical output because the large number of reductant molecules was hindered by the dye molecules reaching the electrode in the desired time limit. Surfactant Tween 80 was used in both photogalvanic cell systems. The concentration of surfactant was kept 1.3×10^{-3} M and 1.2×10^{-3} M in Bromocresol green-EDTA-Tween-80 and naphthol blue black-EDTA-Tween-80. The electrical output of the cell increased with increasing surfactant concentration, reaching a maximum value. With a further increase in the surfactant concentration, a decrease in the electrical output was observed. The most important properties of micellar systems are their ability to solubilize a variety of molecules and their substantial catalytic effect on many chemical reactions. The photogalvanic cell exhibited a better electrical output at the critical micelle concentration of the surfactant. Photoinduced electron transfer processes in micellar systems are potentially important for efficient energy conversion and storage because surfactants help achieve separate photoproducts via hydrophilic-hydrophobic interactions of the products with the micellar interface. Micelles not only solubilized the photosensitizer molecules to a maximum extent around their CMC values but also stabilized the photogalvanic cell systems.

Effect of pH

Photogalvanic cells containing the lissamine green B-ascorbic acid-NaLS system, bromocresol green-ascorbic acid-NaLS system, and brilliant blue FCF-ascorbic acid NaLS system were found to be quite sensitive to the pH of the solution. All three systems with three different dyes

were observed to work effectively in the strong alkaline range. The working range for the present study was in the pH range of 11.52-12.80. The potential of the system increased with increasing pH. The potential reached a maximum value for a particular pH and then decreased with further increases in pH. It was observed that the pH for optimum conditions for the reductant was related to its pKa value, that is, the desired pH should be slightly higher than their pKa values ($\text{pH} > \text{pKa}$). This may be due to the availability of the reductant in its anionic form, which is a better donor.

Effect of diffusion length and electrode area

The diffusion length (i.e., the distance between the SCE and platinum electrode) greatly affects all three systems. The effect of the variation in diffusion length on the electrical output (i_{max} , i_{eq}) and initial rate of generation of current of the photogalvanic cell was observed using H-cells of different dimensions. In the first few minutes of illumination, a sharp increase in the photocurrent was observed, followed by a gradual decrease to a stable photocurrent value. This photocurrent behavior indicates an initial rapid reaction, followed by a slow rate-determining step. The results are also discussed to identify the electroactive species by considering various probable processes and combinations of electroactive species for the electrical output of the photogalvanic cells. The processes and combinations are summarized in Table 1. If the oxidized form of the reductant is formed only in the illuminated chamber and is considered to be the electroactive species in the dark chamber, it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. Consequently, the maximum photocurrent (i_{max}) and rate of photocurrent generation should decrease with an increase in the diffusion length; however, this was not observed experimentally. The value of (i_{eq}) was also observed to be independent of the change in the diffusion length (it decreases slightly). Based on the effect of diffusion path length on the current parameters, it may be concluded that the main electroactive species are the leuco or semi-leuco form of dye (photosensitizers) and the dye in the illuminated and dark chambers, respectively. However, the reductant and its oxidized product act only as electron carriers in this pathway. The effect of the electrode area on the current parameters was also observed in the two systems, and the observations are listed in Table 2. Based on observations, the maximum photocurrent (i_{max}) was found to increase with increasing electrode area, but the equilibrium photocurrent (i_{eq}) was affected slightly, rather it was decreased slightly.

Table 1: Probable process and combinations for electroactive species

In illuminated chamber	In dark chamber
Dye (D)	Oxidized form of the Reductant (R^+)
Semi or Leuco form of the dye (D^-)	Oxidized form of the Reductant (R^+)
Semi or Leuco form of the dye (D^-)	Dye (D)

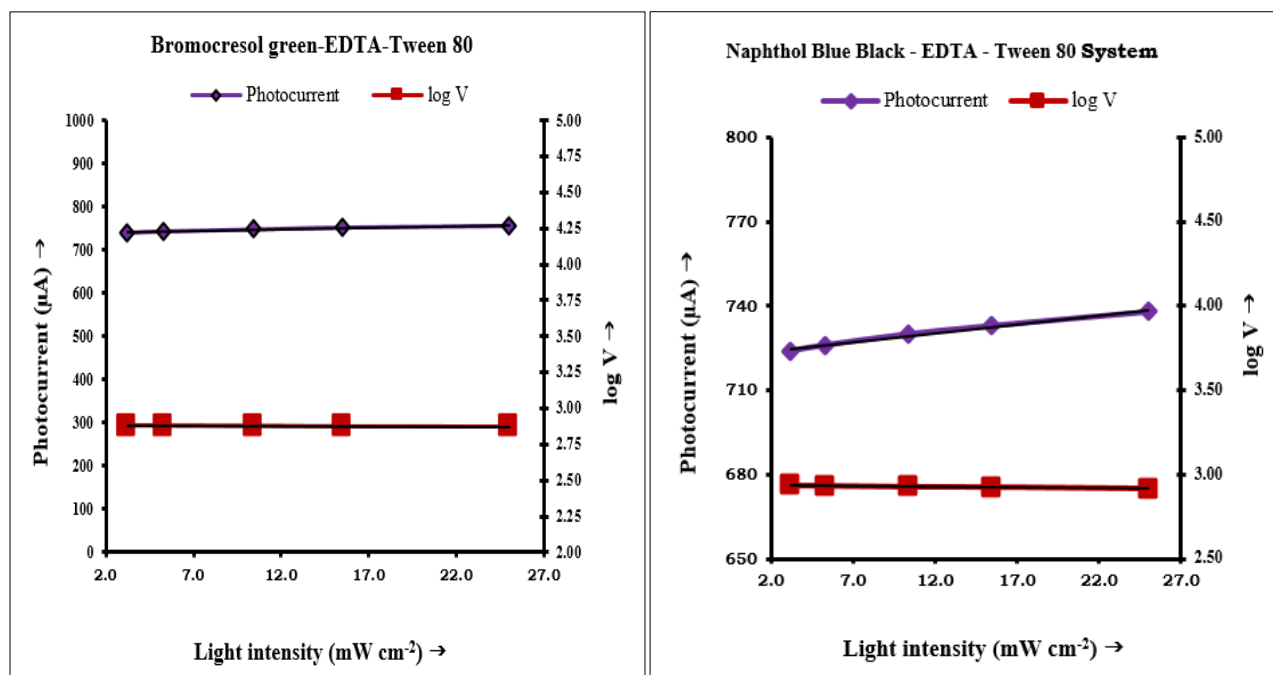
Table 2: Variation of current parameters with electrode area

Electrode Area (cm ²)	System			
	Bromocresol green-EDTA-Tween-80		Naphthol blue black-EDTA-Tween-80	
	I _{max} . in μA	I _{eq} . in μA	I _{max} . in μA	I _{eq} . in μA
0.80	756.0	750.0	760.0	734.0
0.90	757.0	749.0	766.0	733.0
1.0	758.0	748.0	768.0	730.0
1.3	761.0	744.0	770.0	727.0
1.5	763.0	742.0	774.0	720.0
Bromocresol green-EDTA-Tween-80 system				
[Bromocresol green]=2.3 × 10 ⁻⁵ M		Light intensity = 10.4 mW cm ⁻²		
[EDTA] = 1.8 × 10 ⁻³ M		Temperature = 303 K		
[Tween-80] = 1.3 × 10 ⁻³ M		pH = 11.69		
I _{max} = Maximum Photocurrent in μA		I _{eq} . = Equilibrium Photocurrent in μA		
Naphthol blue black-EDTA-Tween-80 system				
[Naphthol blue black]=2.2 × 10 ⁻⁵ M		Light Intensity = 10.4 mW cm ⁻²		
[EDTA]=1.4 × 10 ⁻³ M		Temperature = 303 K		
[Tween-80]=1.2 × 10 ⁻³ M		pH = 11.65		

Effect of light intensity

The intensity of light also affects the electrical output of the cell. The photocurrent exhibited a linear increasing behavior with increasing light intensity, whereas the photopotential

increased logarithmically. This increase in electrical output is due to the increase in the number of photons with increasing light intensity (Fig. 1a and 1b).

**Fig 3:** 1a and 1b: variation of photocurrent and log V with light intensity**Current-voltage properties of the photogalvanic cell:**

The open-circuit voltage (V_{oc}) and short-circuit current (i_{sc}) of the photogalvanic cells were measured under 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 potential and current between these two extreme values (V_{pp} and i_{pp}) were recorded using a carbon pot (log 407 K) connected to the circuit of the microammeter, through which an external load was applied to the circuit. The I-V characteristics of the cells are shown in the current-potential curves (Fig. 2a and b). The i-V curve deviated from its regular rectangular shape. A point in the I-V curve, called the power point, was

determined where the product of the curve of current and potential was maximum. Using the I-V curve, the fill factor was calculated using the following formula:

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

Where,

V_{pp} = Potential at power point (mV) V_{oc} = Open circuit voltage (mV)

i_{pp} = Current at power point (μA) i_{sc} = Short circuit current (μA)

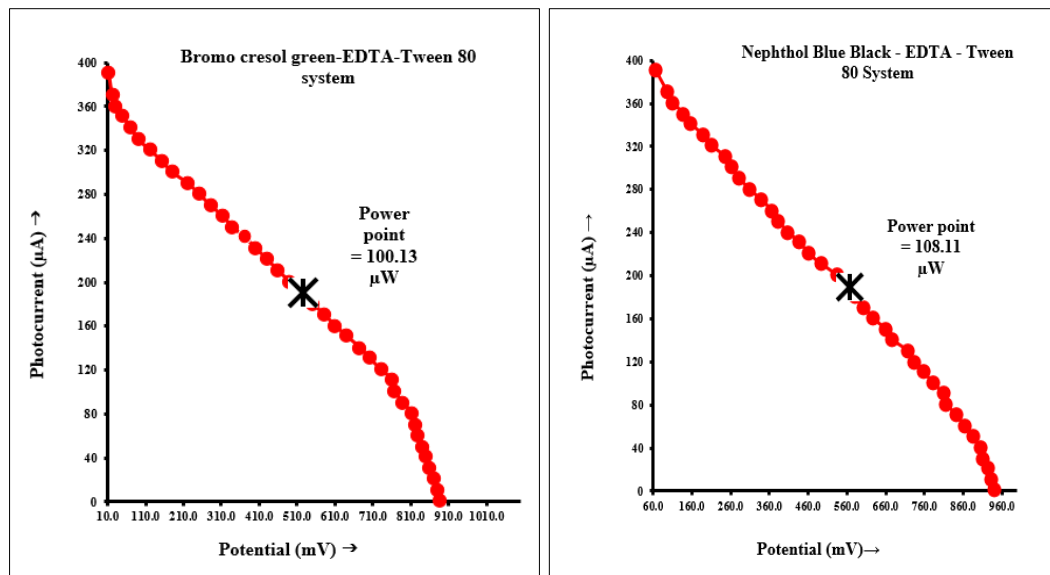


Fig 4: 2a and 2b: Current voltage (i-V) curve of the photogalvanic cell

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 reached a constant value. The performance was determined in terms of the $t_{1/2}$, that is, the time required for the output (power) to fall to half its value at the power point. The overall comparative performance of the photogalvanic cells was observed and reached a remarkable level with respect to the electrical output, initial generation of photocurrent, conversion efficiency, and storage capacity of the photogalvanic cell. The comparative performance obtained in both systems is summarized in Table 3 and graphically shown in the time-power curves (Fig. 3a and 3b).

The conversion efficiency of the cell was determined using the following formula:

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

Where, An electrode area of Pt-foil electrode

Table 3: Comparison of photoelectric parameters of two photogalvanic cell systems

S.No	Electrical Parameters	Observed values of the system	
		Bromocresol green- EDTA - Tween 80	Naphthol blue black-EDTA- Tween 80
1.	Open Circuit Voltage, V_{OC} (mV)	887.0	942.0
2.	Photopotential, ΔV (mV)	760.0	844.0
3.	Short Circuit current, i_{sc} (μA)	748.0	730.0
4.	Current at power point, i_{pp} (μA)	190.0	190.0
5.	Potential at Power point, V_{pp} (mV)	527.0	569.0
6.	Power at Power Point (μW)	100.13	108.11
7.	Charging Time (min.)	75.00	85.00
8.	Fill factor (η)	0.1509	0.1572
9.	Conversion Efficiency (%)	0.96	1.03
10.	$t_{1/2}$ (minutes)	100.0	110.0

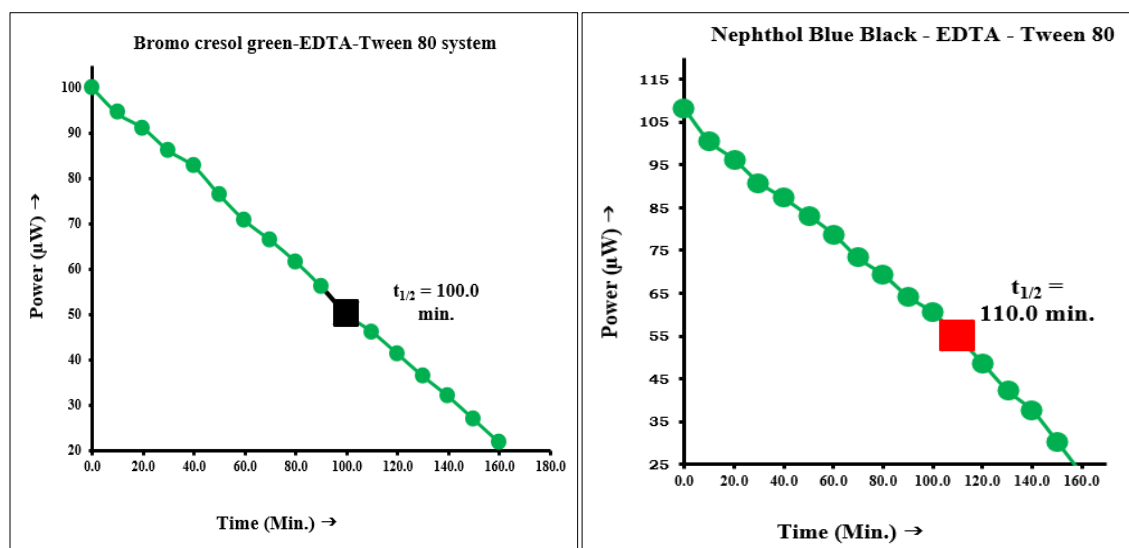


Fig 5: 3a and 3b: Time power curve of the photogalvanic cell systems

4. Mechanism of the photogalvanic cell

When certain dyes are excited by light in the presence of an electron-donating substance (reductant), they rapidly change into a colorless form. The dye now acts as a powerful

reducing agent, donating electrons to other substances and being reconverted to its oxidized state. A schematic of the mechanism is shown in Fig. 4.

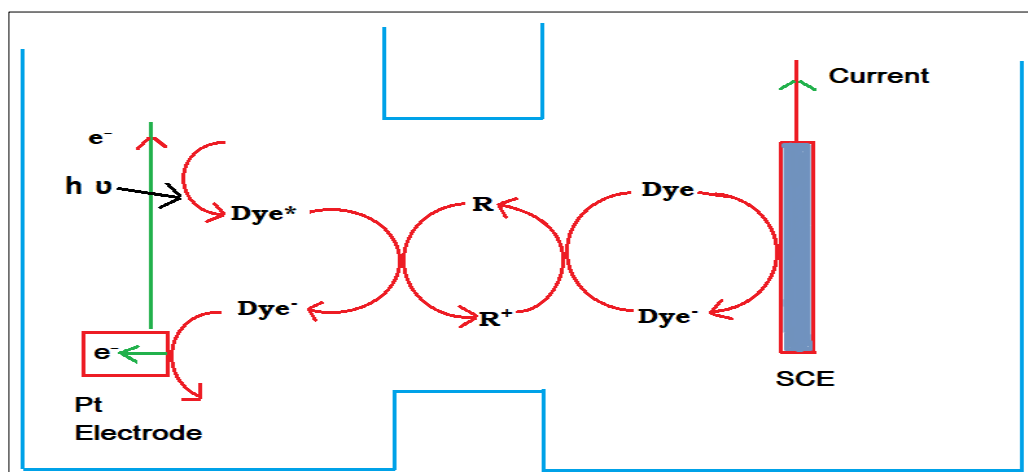


Fig 6: Scheme of mechanism

Illuminated chamber

Irradiation causes the dye molecules to become excited. Both the excited dye molecules and the reductant are transformed into their excited forms when the excited dye molecules absorb an electron from the reductant and change into the semi- or leuco-form of the dye. At the platinum electrode, the semi- or leuco form of the dye loses an electron and is transformed into the original dye molecule.

Dark chamber

At the calomel electrode, the dye molecule absorbs an electron from the electrode and is transformed into a semi- or leuco-form. Finally, the leuco/semi form of the dye and the oxidized form of the reductant mix to generate the original molecules of the dye and the reductant. This cycle of the mechanism is repeated, resulting in the continuous generation of current.

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