



Photogalvanic effect of Mordant red-3 photosensitizer based Photogalvanic Solar Cell in artificial light for simultaneously solar energy conversion and storage

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ABSTRACT:

Dye sensitized solar cells are expected to be one of the efficient 3rd generation solar cells that are generating green energy at low production cost. Since no expensive equipment are required in their fabrication. In this paper review of the structure and operation principles of the Mordant red-3 dye sensitized solar cell is outlined. The main objective of this work is to harness and store the solar energy through Mordant red-3- Ascorbic acid-Ammonium dodecyl sulphate photogalvanic cell. This in alkaline medium has shown hopeful and very effective improvement in solar energy conversion and storage. The solar conversion efficiency, fill factor, cell performance (as $t_{1/2}$), power at power point and equilibrium current at 10.4 mWcm⁻² has been observed of the order of 1.42 %, 0.1183, 120 min, 147.69 μW and 1234 μA respectively.

Introduction

Renewable energy is energy obtained from sources that are essentially inexhaustible and it can be harnessed without release of harmful pollutants. Harnessing energy from sun light is so far considered as one of the effective solutions in generating green energy. Solar cells are the basic block of solar array where the absorption of light quanta of specific energy results in generation of charge carriers. The photo generated charge carriers deliver their energy to some external load where it converted to any other desirable energy form. Photogalvanic (PG) cell is a liquid phase dye sensitized solar cell which converts the solar energy into electrical energy. These cells are based on the photo-galvanic effect (PGE). PGE is a special type of photochemical and photoelectric processes occur on the surface layer of the electrode.¹ The PGE was first observed in the action of light on the equilibrium of ferrous iodine-iodide.² This effect was

systematically studied in thionine-Fe system by Rabinowitch,³ who suggested that the PGE could be used for solar energy conversion and storage. The PGE in the Amino black 10B-Tween 60-Ascorbic acid system and the Bromo cresol purple-Tween 60-Ascorbic acid system has been investigated by Sagar and Genwa⁴⁻⁵. Chauhan and Genwa⁶⁻⁷ have observed PGE in several novel photogalvanic cells in view of electrical characteristics and solar energy conversion and storage. Bhimwal and Gangotri⁸ have employed a photogalvanic system that includes methyl orange, D-xylose, and Sodium Lauryl Sulphate chemicals. The observed values of the power at the power point, conversion efficiency, fill factor, and the rate of initial generation of the photocurrent were as follows: 168.95 μW, 1.6245%, 0.3214, and 69.44 μA min⁻¹, respectively. Gangotri and Bhati⁹ have used Sodium Lauryl Sulphate (SLS) and methylene blue two chemicals in their photogalvanic cells for electrical production. According to Meena and Chandra.¹⁰⁻¹¹ solar cells



comprising of photosensitizer-reductant for the production of electrical energy were successfully created. Brilliant cresyl blue (BCB)-fructose and Rodamine B - fructose systems were employed by Sharma et al.¹²⁻¹³ in order to improve the

Table – 1

System	Max ^m potential (mV)	Max ^m photocurrent (μ A)	Isc (μ A)	Power point (μ W)	Conversion efficiency (%)	Fill factor (η)	Storage capacity (min)
BCBFructose	1115	785	590	183.3	1.9586	----	228
RDBFructose	1071	1049	972	244.02	7.58	----	216

The Bismark brown-Oxalic acid system, which was given by Nenival, demonstrates the effect of the reductant in the photosensitizer on the conversion and storage of solar energy.¹⁴ The photogalvanic cell formed with DTPA-Acridine orange-Sodium lauryl sulphate system was studied by Genwa and Kumar.¹⁵ The system produced a photopotential of 746.0 mV and a photocurrent of 205.0 A correspondingly. The photogalvanic effect was investigated by Genwa et al.¹⁶ using a photogalvanic cell that also included an ascorbic acid and methylene blue system. The photocurrent and photopotential that were produced by the

Table – 2

System	Photopotential (mV)	photocurrent (μ A)	Conversion eff.(%)	Fill factor (η)	Storage capacity(min)
LGB-AA-SLS	850.0	375.0	1.0257	0.2598	170.0
BCG-AA-SLS	834	350.0	0.80	0.23	140.0

Genwa and Sagar²⁰ investigated the photogalvanic behaviour in a system consisting of Xylidineponceau, Tween 60, and ascorbic acid. Under perfect circumstances, the greatest power that may be generated by a cell is 68.77 microwatts.

Table – 3

System	Photopotential (mV)	photocurrent (μ A)	Conversion efficiency (%)	Fill factor (η)	Storage capacity (min)
Trypan-Arabinose	834.0	350.0	0.80	0.23	140.0
NileblueArabinose	816.0	330.0	0.6095	0.2566	120.0

solar energy conversion and storage capacity of photogalvanic solar cells. In this study, the observed values of electrical parameters are given in bellow table 1.

cell came in at 165.0 μ A and 901.0 mV, respectively. For the purpose of converting solar energy into usable form and storing it, Genwa and Chauhan¹⁷ have designed a photogalvanic system that includes the chemicals Brilliant black, Ammonium lauryl sulphate, and EDTA. In a cell containing Lissamine green B (LGB)-Ascorbic acid (AA)-sodium lauryl sulphate and Bromocresol green (BCG)-ascorbic acid (AA)-SLS System, Genwa and Singh¹⁸⁻¹⁹ discovered a photogalvanic effect. The generated photopotential, photocurrent, conversion efficiency, fill factor and storage capacity are given below table 2:

The photogalvanic effect has been seen by Gangotri and Mohan²¹⁻²² in cells that have the Trypan blue- Arabinose and Nile blue- Arabinose systems. The results are shown in the following table 3.



Gangotri and Koli²³ have worked on modified photogalvanic cell fabricated with safranin O–sodium lauryl sulphate-EDTA chemical system in order to increase the solar power generation and storage. The redesigned cell had significantly improved performance when measured in terms of charging time (40 minutes), initial production of photocurrent (260 $\mu\text{A min}^{-1}$), equilibrium photocurrent (1700 μA), power (364.7 μW), half change time (40 minutes), and efficiency (8.93%). In order to make photogalvanic cell more environmental friendly and sustainable by the P. Koli²⁴ has been researched on the use of natural and renewable substances as photosensitizer. The obtained cell performance is extremely promising to photogalvanics (Open-circuit potential 1050 mV, charging time 18 minutes, Short-circuit current (i_{sc}) 1750 μA , power 384.0 μW , storage capacity as half change time $t_{0.5}$ 44 minutes, conversion efficiency 9.22%). This research demonstrates that natural resources, such as crude spinach extract, can also be used to sensitize photogalvanics with an efficiency that is comparable to that of synthetic dye sensitizers. In addition, natural resource sensitizers have the advantages of being inexpensive and free from the pollution that is associated with the production and disposal of dyes. Metanil yellow dye has been used as a photosensitizer with sodium lauryl sulphate surfactant by P. Koli²⁵ in order to improve the conversion efficiency of the photogalvanic cells convert solar energy and the amount of energy can store. According to the findings of this study, the electrical performance was significantly improved, with values reported for power at power point 822 mW, equilibrium photocurrent (i_{sc}) 6000 mA, photopotential (V_{oc}) 1110 mV, conversion efficiency 20.41 percent, and storage capacity $t_{0.5}$ 105 minutes. An investigation on the photogalvanic effect was carried out using a Janus green B-DSS-EDTA system. As a reductant, EDTA is employed in this process, while the azo dye Janus green B are used as photo sensitizers. In aqueous solution the chemical compound known as dioctyl sodium sulphosuccinate (DSS) functions as a surfactant. Electrical parameters such as photopotential and photocurrent are produced in the amount of 930 mV and 435 μA , respectively. At its power point, the system is capable of producing power equal to 164.1 microwatts. The fill factor for the system is 0.33, while the system's conversion efficiency is 1.58%. In the dark, the cell operates for 180

minutes (Rathore and Singh).²⁶The scientific society has used various photosensitizers, surfactants, reductants in photogalvanic cells to convert solar energy into electrical energy, but no attention has been paid to the use of Mordant red-3dye as energy material to increase the electrical output and performance of the photogalvanic cell. Therefore, present work has been done to obtain better performance and commercial viability of the photogalvanic cell.

Result and discussion

Effect of variation of Mordant red-3, Ascorbic acid and Ammonium dodecyl sulphate concentration:

The effect of variation of Mordant red-3, Ascorbic acid and Ammonium dodecyl sulphate concentration are given in table 4. Variation of dye concentration studied by using solution of Mordant red-3 of different concentrations. It was observed that the photopotential, photocurrent and power enhanced with enhancing in concentration of the dye [Mordant red-3]. A maximum was obtained for a particular value of dye concentration (24×10^{-6} M), above which shortage in electrical output of the cell was observed. The low electrical output observed in the low concentration range of the dye due to the limited number of dye molecules to absorb most of the light in the path, while the high density of the dye also resulted in a decrease in output due to light intensity reaching the molecule near electrode decrease due to the absorption of a large portion of light by dye molecules present in the path, therefore corresponding fall in the electric output. With increasing the dose of reductant [Ascorbic acid], the photopotential, photocurrent and power were found to increase till it reaches a maximum value at 13×10^{-4} M. On further increasing the Ascorbic acid dose, fall in output was observed. Decreased energy output also resulted in a reduction in reductant dose due to the small number of molecules available to donate electrons to dye molecule. On the other hand, the movement of dye molecules is prevented by the high concentration of reductant in order to reach the electrode at the desired time limit and will lead to a decrease in electrical output. The electrical output of the cell increased in increasing the concentration of surfactant [ADS]. A maxima was obtained at a certain value (15×10^{-4} M) of concentration of Sodium lauryl sulphate. On further increasing the surfactant concentration it react as a barrier and major portion of the



surfactant photo bleach the less number of dye molecules so that a down fall in electrical output was observed.

Effect of variation of pH:

Photogalvanic cell containing Mordant red-3- Ascorbic acid- ADS system was found to be very sensitive to the pH of the solution. It has been observed that there is an increase in photopotential, photocurrent and power with an increase in pH value (Alkaline range). At pH 11.57 a maxima was obtained (839 mV, 1234 μ A and 1035.33 μ W). With an 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 donor form of reductants at that pH value. The results showing the pH effect are summarized in table 5.

Effect of diffusion length and electrode area:

The effect of variation of diffusion length (distance between two electrodes) on the current parameters of the cell (i_{max} , i_{eq} and initial rate of generation of photocurrent) was investigated using H-shaped cells of different dimensions. It was noted that in the first few minutes of illuminations there was sharp increase in photocurrent. As consequences, the maximum photocurrent (i_{max}) increase in diffusion length because path for photochemical reaction was increased, but this is not detected experimentally. Whereas equilibrium photocurrent (i_{eq}) decreased linearly. Therefore, it may be concluded that the main electroactive species are the leuco or semi form of dye (photosensitizer) in the illuminated and dark chamber respectively. The results are summarized in table 6. The effect of electrode area on the current parameters of the cell was also studied. It was noted that with the increase in the electrode area the value of maximum photocurrent (i_{max}) is found to increase. Results are summarized in table 7.

Current-Voltage (i-V) characteristics of the cell:

The short circuit current (i_{sc}) 1234 μ A and open circuit voltage (V_{oc}) 1011 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 Mordant red-3 - Ascorbic acid- ADS system is graphically shown in Fig.1 and summarized in table 8. 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}) 271 μ A and potential (v_{pp}) 545mV was maximum. With the help of i-V curve, the fill-factor was calculated as 0.1073 using the formula:

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

Cell performance and conversion efficiency:

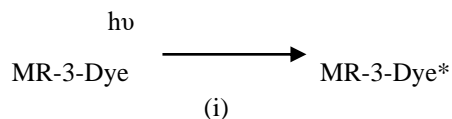
The performance of the photogalvanic cell was observed by applying an external load (necessary to have current at power point) after termination the illumination as soon as the potential reaches a constant value. The performance was determined in terms of $t_{1/2}$, i.e., the time required in fall of the output (power) to its half at power point in dark. It was observed that the cell containing Mordant red-3 - Ascorbic acid- ADS system can be used in dark for 120.0 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 1.42% using the formula. The results are graphically represented in time-power curve (Fig. 2).

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

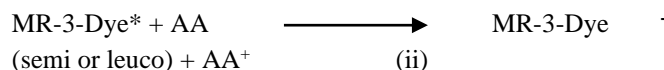
Mechanism:

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

Illuminated chamber: On irradiation, dye molecules get excited.

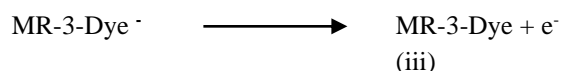


The excited MR-3 dye molecules accept an electron from ascorbic acid and converted into semi or leuco form.



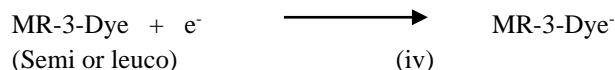
At platinum electrode:

The semi or leuco form of MR-3 dye loses an electron and converted into original MR-3 dye molecule.



Dark Chamber:

At counter electrode:



Finally leuco/semi form of MR-3dye and oxidized form of ascorbic acid combine to give original MR-3dye and ascorbic acid molecule. This cycle of mechanism is repeated again and again leading production of current continuously.



Here MR-3-Dye, MR-3-Dye*, MR-3-Dye⁻, AA and AA⁺ are the dye, its excited form, leuco form, Ascorbic acid (reductant) and its oxidized form, respectively. The scheme of mechanism is shown in fig.3

Materials and methods:

Mordant red-3, Ascorbic acid, Ammonium dodecyl sulphate and NaOH of Lobachemie were used in the present work. Solutions of ascorbic acid, Mordant red-3 (Scheme 1), Ammonium dodecyl sulphate (Scheme 2) and NaOH (1N) were prepared in double distilled water (conductivity $3.5 \times 10^{-5} \text{ Sm}^{-1}$) and kept in amber coloured containers to protect them from sun light. 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 to unaffected

from sun radiation. A shiny platinum 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. Platinum electrode act 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 4.

Conclusions:

India has a severe electricity shortage. It needs massive additions in capacity to meet the demand of its rapidly growing economy. Development of solar energy, which is indigenous and distributed and has low marginal cost of generation, can increase energy security by diversifying supply, reducing import dependence, and mitigating fuel price volatility. Solar energy development in India can also be an important tool for promoting regional economic development, particularly for many underdeveloped states, which have the greatest potential for developing solar power systems which is unlimited and clean source of energy. It can provide secure electricity supply to foster domestic industrial development. So it can be concluded that the photogalvanic cell have inbuilt storage capacity and stored energy can be used in absence of light, photogalvanic cells are favourable because low cost materials are used in these cells. The conversion efficiency, storage capacity, power at power point and fill factor are recorded as 1.42%, $t_{1/2} 120.0 \text{ min}$, $147.69 \mu\text{W}$ and 0.1183 respectively in Mordant red-3 - Ascorbic acid-ADS system.

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**Table -4. Effect of variation of Mordant red-3, Ascorbic acid and ADS concentrations**Light Intensity = 10.4 mW cm⁻², Temperature = 303 K, pH = 11.57

Concentrations	Photopotential (mV)	Photocurrent (μA)	Power (μW)
[Mordant red-3] × 10⁻⁶ M			
21	538	901	484.738
23	757	1131	856.167
24	839	1234	1035.326
26	761	1110	844.71
27	535	879	470.265
[Ascorbic acid] × 10⁻⁴ M			
9	553	887	490.51
11	663	1105	732.62
13	839	1234	1035.33
14	678	1079	731.56
15	555	889	493.40
[ADS] × 10⁻⁴ M			
12	627	852	534.20
13	754	1083	816.58
15	839	1234	1035.33
16	777	996	773.89
18	633	851	538.68

Table -5 Effect of Variation of pH

pH	Photopotential (mV)	Photocurrent (μA)	Power (μW)
11.53	539	837	451.14
11.55	653	935	610.56
11.57	839	1234	1035.33
11.59	658	962	633.00
11.6	534	819	437.35

Table- 6 Effect of Diffusion Length

Diffusion Length DL (mm)	Maximum Photocurrent i _{max} (μA)	Equilibrium Photocurrent i _{eq} (μA)	Rate of initial Generation of Current (μA min ⁻¹)
35.0	1288.0	1241.0	33.89
40.0	1293.0	1239.0	34.03
45.0	1299.0	1234.0	34.18



50.0	1303.0	1231.0	34.29
55.0	1307.0	1227.0	34.39

Table - 7 Effect of Electrode Area

Electrode Area (cm ²)	Maximum photocurrent <i>i</i> _{max} (μA)	Equilibrium photocurrent <i>i</i> _{eq} (μA)
0.70	1287	1242
0.80	1291	1239
1.00	1299	1234
1.20	1305	1226
1.30	1309	1223

Table-8 Current-Voltage (i-V) characteristics of the cell

Time(min.)	Photopotential(mV)	Photocurrent(μA)	Power point(μW)
5	1011	0	0
10	981	10	9.81
15	970	30	29.1
20	909	69	62.721
25	837	94	78.678
30	829	104	86.216
35	794	114	90.516
40	697	171	119.19
45	670	181	121.27
50	545	271	147.7
55	528	278	146.78
60	467	314	146.64
65	371	374	138.75
70	323	429	138.57
75	273	464	126.67
80	262	479	125.5
85	157	579	90.903
90	109	609	66.381
95	79	629	49.691

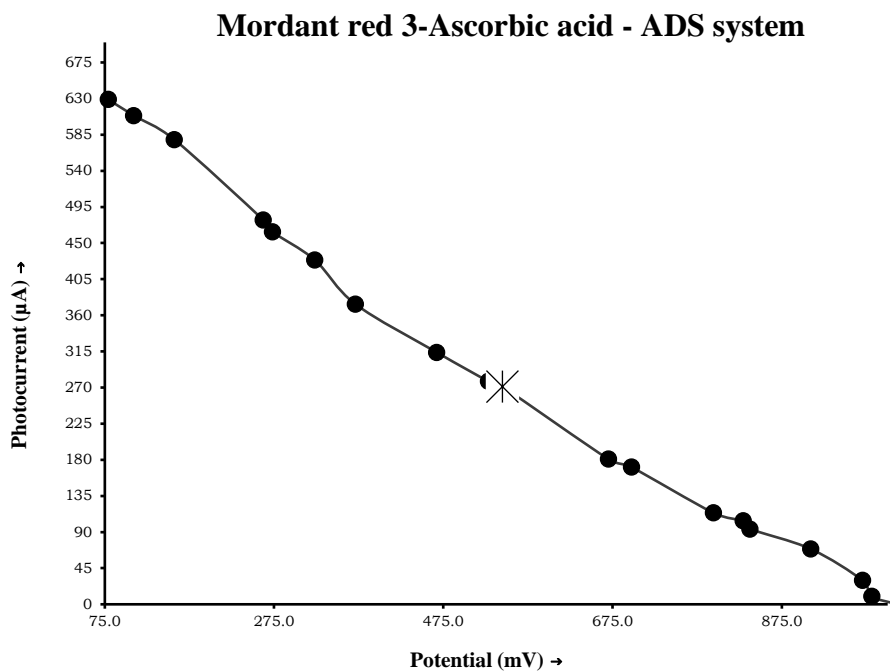


Fig. 1 CURRENT VOLTAGE (i-V) CURVE OF THE CELL

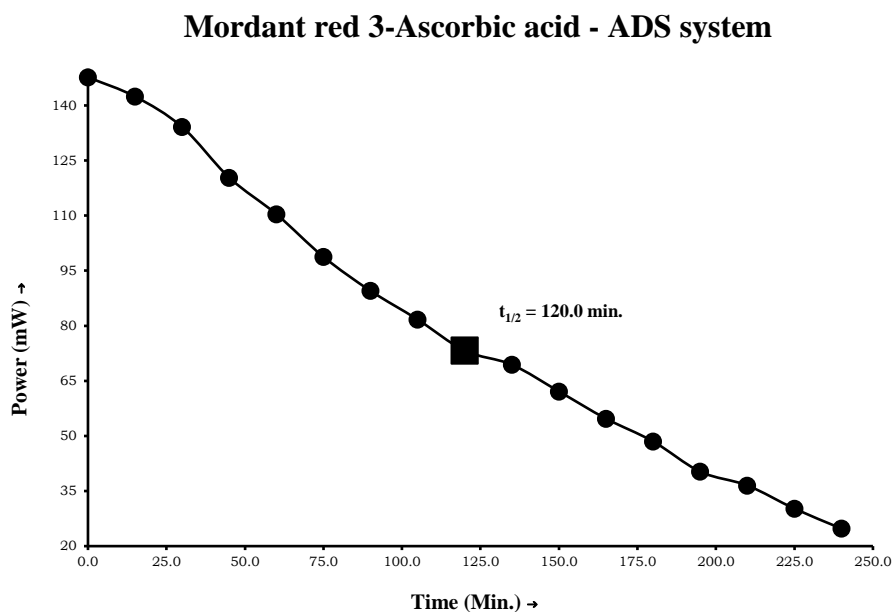


Fig. 2 TIME-POWER CURVE OF THE CELL

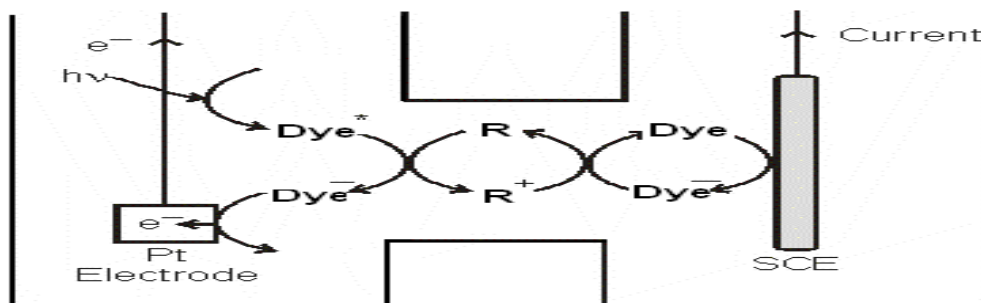


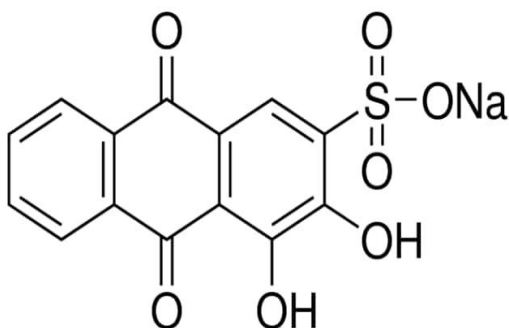
Fig. 3 SCHEME OF MECHANISM

SCE = Saturated calomel electrode

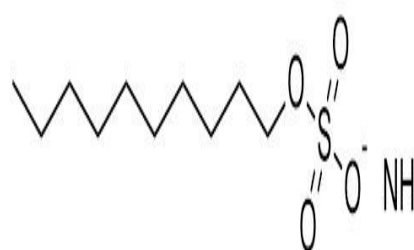
R = Reductant

D = Dye (Photosensitizer)

D = Semi & Leuco form



Scheme 1. Mordant red-3



Scheme 2. Ammonium dodecyl sulphate

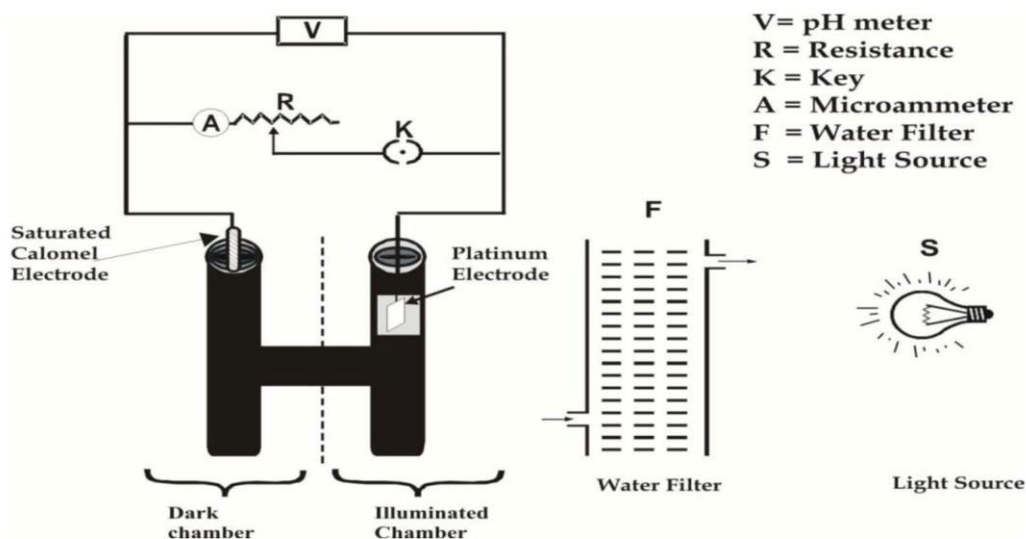


Fig.4 PHOTOGALVANIC CELL SET-UP



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