



## USE OF ACID RED-36 DYE AS PHOTOSENSITIZER IN PHOTOGALVANIC CELL FOR SOLAR ENERGY CONVERSION AND STORAGE

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### ABSTRACT

Acid red-36 dye was used as photosensitizer with EDTA in alkaline medium to enhance the performance of photogalvanic solar cell for its commercial viability. In this study, the obtained cell performance in terms of storage capacity (as half life) was 160 min in dark upon irradiation for 180 min. The photopotential, photocurrent, power at power point, fill factor and conversion efficiency were 685 mV, 230 $\mu$ A, 71.50 $\mu$ W, 0.45 and 2.75 %, respectively. The effect of variation of different parameters like concentration of dye, reductant concentration, pH, light intensity, electrode area, diffusion length are observed. A current-voltage (i-V) characteristics of the cell and variation of pH during illumination was studied. It was observed that the pH of solution decrease during illumination of cell.

**Keywords:** Acid red-36, Photogalvanic cell, Storage capacity, Conversion efficiency, Current-voltage characteristics.

### 1. INTRODUCTION

Today, global warming and rapid decrease in energy resources caused by the large scale consumption of fossil fuels have become serious challenge to human being. Renewable energy resources are attracting a great deal of attention, and solar energy is one of the most hopeful future energy resources. The photochemical invention of electricity has attracted the attention of researchers as a feasible media for solar energy conversion. The photogalvanic solar cells are photo electrochemical instrument which are capable of simultaneous solar power generation and storage. The photogalvanic cells are based on the photogalvanic effect which was first time discovered in 1925 by Radial and Williams [1] and systematically studied by Rabinowitch. The photogalvanic effect is just like as Becquerel effect (in Becquerel effect, the photochemical or photoelectric process takes place at the surface layers of the electrodes) [2]. After the systematic study of photogalvanic effect, an idea was caught by researchers that this photogalvanic effect may be used for solar energy conversion and storage. To put this idea in to the research, many research studies on photogalvanic cell systems have been reported.

The photogalvanic cell is one of the best examples of the photoelectrochemical device in which both electrodes

(anode and cathode) are dipped in the alkaline solution of photosensitizer and reductant. Various photosensitizers like Methyl Violet [5], Methylene blue [6, 7], Bibrich Scarlet [8], Rose Bengal [9], Eosin [10], Azure-B [11], Azur-A [12], Brilliant Cresyl Blue [13], Rhodamine-B [14], Safranin [15]-[17], Bromocresol green [18], etc.; various inorganic and organic reductants like iron [3], Oxalic acid [7], D-xylose [9], ethylenediaminetetraacetic acid (EDTA) [11, 12], fructose [13, 14], ascorbic acid [18-20], arabinose [21], etc. have been reported for the solar energy conversion and storage in photogalvanic cells. A survey of literature has revealed that the optimum electrical cell performance is depended on the variables like concentration of photosensitizer(s), reductant(s), and pH of the solution. Therefore, to improve the performance of photogalvanic cells, these variables have to be center of the study. So far, the studies have reported photo-decay of the photosensitizer as one of the hurdles for the low cell efficiency. Therefore, the dye having a stable framework has to be used along with good reductant and surfactant. The acid yellow-36 dye is reported as a good photo-decay resistant dye probably due to strong aromatic bonding difficult to degrade [22]. It is also a low molecular weight and cheap dye having the prospect for higher diffusion (favorable factor for cell performance)

and decrease the cost of cell. The literature survey also reveals that the EDTA is an extremely stable safe organic acid with good reduction capacity for the various dyes. In view of all these facts, the acid yellow-36 -EDTA system have been used to further enhance the performance of photogalvanic cells.

## 2. MATERIAL AND METHODS

### 2.1. Material used

Acid yellow-36, ethylenediaminetetraacetic acid (EDTA), Sodium Hydroxide (NaOH) have been used as photo-sensitizer, reductant, and alkaline medium, respectively. Characteristics of Acid Yellow-36 dye are M.F. C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S, M.W. 375.78,  $\lambda_{\max}$  414 nm, and C.I. No. 13065. The solutions of acid yellow dye (M/100), EDTA (M/100), and NaOH (1M) have been used. All these solutions have been prepared in double distilled water and kept in amber colored vessels to protect them from sunlight.

### 2.2. Experimental setup of photogalvanic cell

The experimental setup consisted of a dark H-shape glass tube with a transparent window in one arm (1.21cm<sup>2</sup>) for illumination. The solution of known amount of the photo sensitizer, EDTA, reductant and NaOH was filled in H-Shape tube. The total volume of the solution was always 30 ml. A platinum electrode (0.25cm<sup>2</sup>) was dipped in one limb of the H-shape tube having a window which acted as illuminated chamber and saturated calomel electrode (SCE) combination with pH electrode was immersed in another limb acted as dark chamber. The terminals of the electrodes were connected to a digital multimeter (KROSS-S DT830D) and digital pH meter (111E) was connected to pH electrode which was in combination with saturated calomel electrode. The photopotential(mV) was measured in dark when the photogalvanic cell attend a stable potential. Then the limb containing transparent window was exposed to the light source *i.e.* a 200W tungsten lamp (Sylvaia). A water baker was sited between the photogalvanic cell and the light source to cut off IR radiations. The photopotential and photocurrent generated by the system was measured by the digital multimeter and microammeter (osaw). The initial pH of solution and change in the pH of solution during illumination was measured by digital pH meter. The current voltage characteristic of photogalvanic cell was studied by applying an external load with the help of carbon pot (log 407K) connected in the circuit through a key. The experimental setup of photogalvanic

cell is shown in fig. 1.

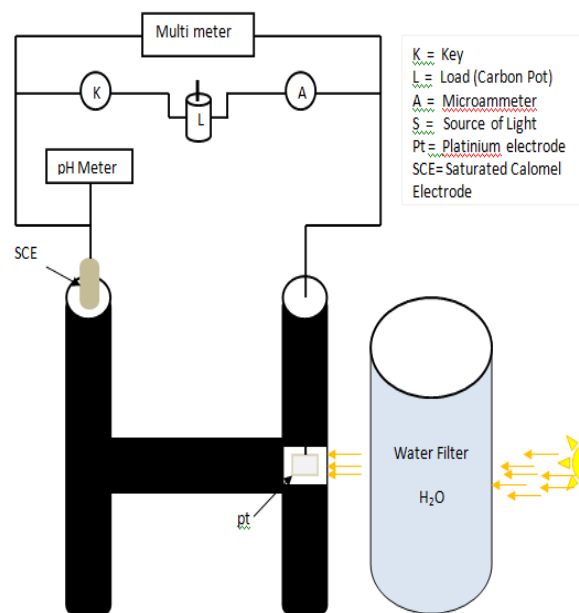
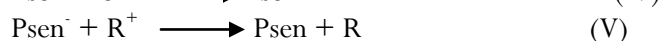
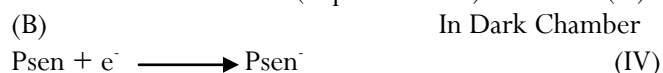
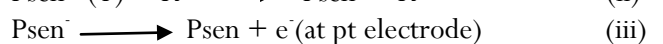
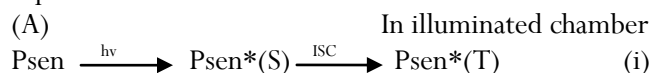


Fig. 1: Experimental Setup of Photogalvanic Cell

### 2.3. Mechanism of current generation

The photogalvanic system acts as a cyclic light-driven electricity generator [22]. In photogalvanic system, reducing agents and their oxidized products are the electron carriers in the alkaline solution of photosensitizer and reductant. The photo current in photo galvanic cell generated by electron exchange among photosensitizer, reductant and electrode can be represented as follows.



Here Psen\*, Psen<sup>-</sup>, R and R<sup>+</sup> are the excited state of photosensitizer, reduced form of photosensitizer, reductant and oxidized form of reductant respectively. (S), (T), and ISC are excited singlet state, excited triplet state of photosensitizer and inter system crossing respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Variation of pH and potential with time during charging of cell

The pH of solution in each photogalvanic cell continuously decreased during charging of cell and

became quite constant after some time. The reason for this observation may be the OH<sup>-</sup> ions are continuously combine with cationic (oxidized) form of reductant (R<sup>+</sup>). The photopotential of each photogalvanic cell increase regularly and reach to a highest value (V<sub>max</sub>) which then decrease and become quite constant after some time. The variation of photopotential with time of photogalvanic cell consisting 1.2 ml of M/100Dye (Acid Yellow-36) solution, 2.2 ml of M/100 EDTA, 3.8 ml of 1 M NaOH and 22.8 ml of doubly distilled water (to make volume of solution 30 ml) is shown in fig. 2.

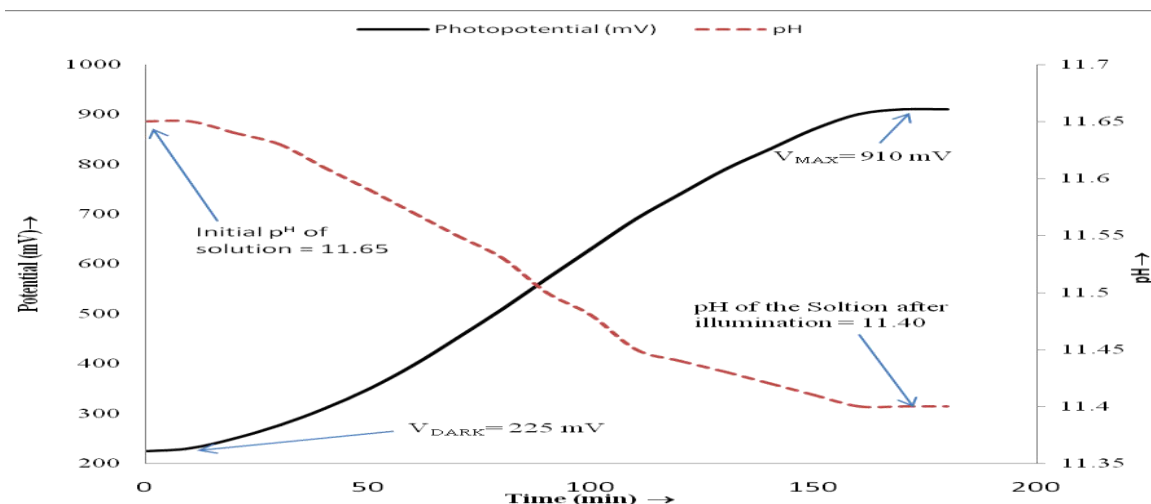
**3.2. i-V Characteristic of the Cell**

The power of the cell is taken as the product of current and corresponding potential. When potential is highest (V<sub>OC</sub>) at open circuit condition the current is zero the power also zero. When current is highest (i<sub>SC</sub>) at closed

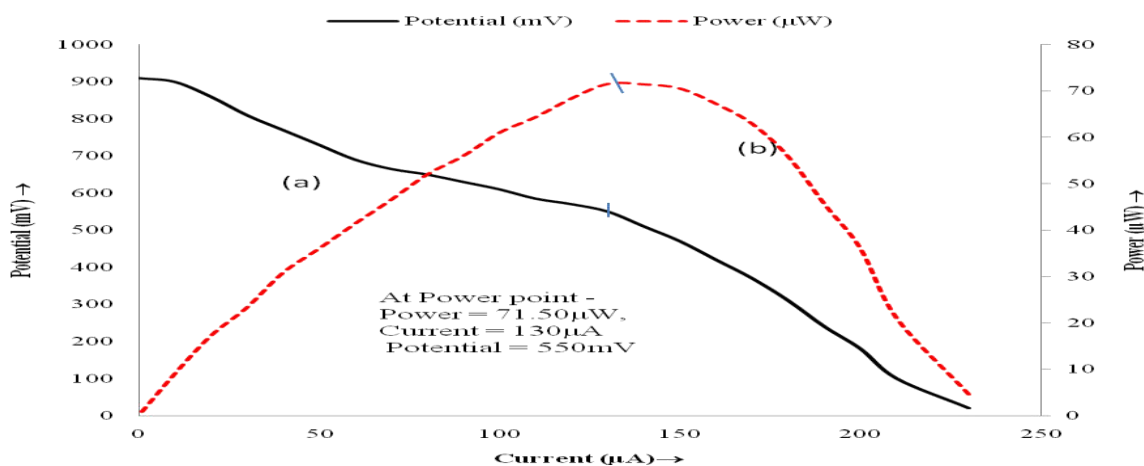
circuit condition the power is nearly zero due to nearly zero potential. There is inversely relation between current and potential. The extreme current (i<sub>pp</sub>) and potential (V<sub>pp</sub>) is obtained by applying resistance in circuit with the help of carbon pot (log 470 K) at which the power of cell is maximum this point is power point shown in fig. 3. The fill factor and conversion efficiency of photo galvanic cell consisting 1.2 ml of M/100Dye (Acid Yellow-36) solution, 2.2 ml of M/100 EDTA, 3.8 ml of 1 M NaOH and 22.8 ml of doubly distilled water (to make volume of solution 30 ml) has been calculated as 0.45 and 2.75 % respectively using following equations.

$$\text{Fill factor (FF)} = V_{pp} \times i_{pp} / V_{OC} \times i_{SC} \tag{VI}$$

$$\text{Conversion efficiency} = V_{pp} \times i_{pp} \times 100 / \text{Electrode Area} (0.25 \text{ cm}^2) \times 10.4 \text{ mWcm}^{-2} \tag{VII}$$



**Fig. 2: Variation of pH and Potential with Time During Charging of Cell<sup>a</sup>**



**Fig. 3: Variation of Potential and Power with Current<sup>a</sup> (a) i-V Characteristic of the Cell, (b) Power vs Current**

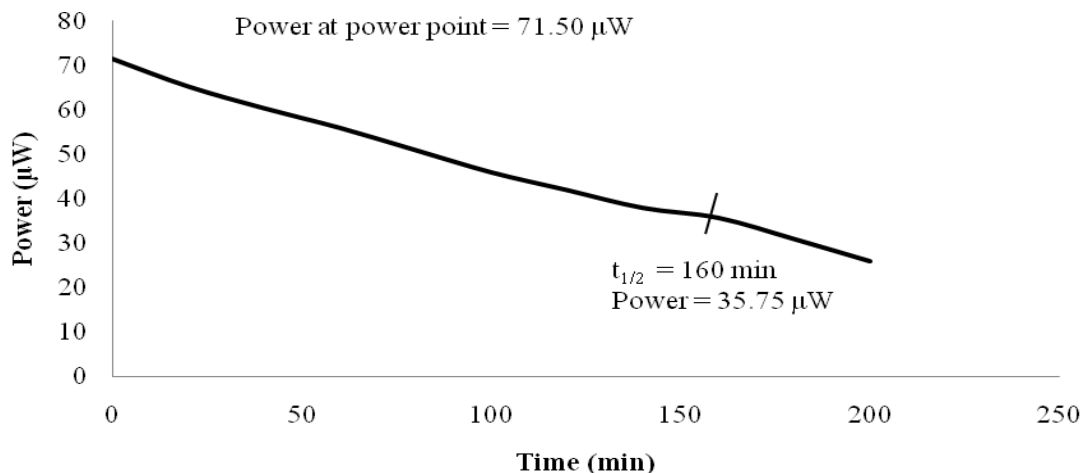
### 3.3. Storage capacity of the cell

During study of cell performance (in term of  $t_{1/2}$  i.e. time required in fall of maximum power, power at power point to its half in dark) in absence of illumination, the power decrease with time, because the number of available sensitizer molecules in reduced form (having excess electron) undergoing oxidation by transferring their excess electron to pt electrode decrease with time. It is observed that the half life ( $t_{1/2}$ ) of the photogalvanic cell in present work is 160 min with 1.2 ml of M/100Dye (Acid Yellow-36) solution, 2.2 ml of M/100 EDTA, 3.8 ml of 1 M NaOH and 22.8 ml of doubly distilled water (Fig. 4). The storage capacity of a photogalvanic cell can not be unlimited because the life time of the reduced excited state of any photosensitizer is not infinite in the dark. In the present work, the storage capacity of the cell is very high because the reduced molecules of excited photosensitizer are more stable in comparison with all dye based photogalvanic system reported earlier.

### 3.4. Effect of Dye (Acid yellow-36) Concentration on Cell Parameters

The effects of dye concentration on cell performance have been studied having all factors common except photosensitizer quantity. Each cell having total 30 ml of solution including Acid yellow-36 (different in each cell), 2.2ml EDTA, 3.8 ml NaOH and doubly distilled water was taken as much as to make total volume of solution equal to 30 ml. Increase in photopotential and photocurrent with increase in concentration of Acid yellow -36 up to  $4 \times 10^{-4}$  M and beyond this concentration the decrease in potential and current are found (Table 1).

Only the particles of dye, attached at front surface of pt electrode are responsible for cell output. At low concentration, less number of dye molecules at pt electrode to absorb photons and high concentration of dye molecules does not permit the desired light intensity at pt electrode there will be corresponding fall in power of the cell.



<sup>a</sup>At [EDTA] =  $7.33 \times 10^{-4}$  M, pH = 11.65, [Acid Yellow-36] =  $4.0 \times 10^{-4}$  M,  $T_{em} = 300$  K, Light intensity =  $10.4 \text{ mW cm}^{-2}$ , electrode area =  $0.25 \text{ cm}^2$ , Diffusion length = 5.3 cm

Fig. 4: Study of Half Life of the Cell<sup>a</sup>

Table 1: Effect of dye concentration [Acid yellow-36] on cell parameters<sup>b</sup>

[Acid Yellow-36] $\times 10^{-4}$ M	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu$ A)	Power at power point ( $\mu$ W)	Fill factor	Conversion efficiency (%)
2.66	648	198	51.24	0.39	1.97
3.33	670	215	62.40	0.43	2.40
4.00	685	230	71.50	0.45	2.75
4.66	673	216	61.20	0.42	2.35
5.33	650	200	52.43	0.40	2.01

<sup>b</sup>At [EDTA] =  $7.33 \times 10^{-4}$  M, pH = 11.65, Temp = 300 K, Light intensity =  $10.4 \text{ mW cm}^{-2}$ , electrode area =  $0.25 \text{ cm}^2$ , Diffusion length = 5.3 cm

### 3.5. Effect of Variation of pH

The effect of variation of pH on the electrical output of cell has been studied having all factors common except NaOH concentration *i.e.* pH. Each cell had 30ml of solution including NaOH (different concentration in different cell), 2.2ml EDTA, 1.2 ml M/100 dye (acid yellow-36) solution and double distilled water was taken as much to make total volume of solution equal to 30 ml.

A general increase in cell parameters like  $V_{OC}$ ,  $I_{SC}$ , and power were observed with increase in pH up to 11.65 and beyond this pH, decrease in the parameters have been found (Table 2). The reason for this observation may be that in alkaline medium easy formation of anionic form of reductant which easily reduce the dye molecules. At high concentration of NaOH *i.e.* at high pH, the  $OH^-$  ions combine with oxidized form of reductant.

**Table 2: Effect of Variation of pH<sup>c</sup>**

pH	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu$ A)	Power at power point( $\mu$ W)	Fill factor	Conversion efficiency (%)
11.54	644	197	50.79	0.40	1.95
11.60	665	210	61.98	0.44	2.38
11.65	685	230	71.50	0.45	2.75
11.71	667	215	62.12	0.43	2.38
11.77	642	205	52.67	0.40	2.02

<sup>c</sup>At  $[EDTA] = 7.33 \times 10^{-4}M$ ,  $[Acid\ Yellow-36] = 4.00 \times 10^{-4}M$  Temp = 300 K, Light intensity =  $10.4\ mW\ cm^{-2}$ , Electrode Area =  $0.25\ cm^2$ , Diffusion length = 5.3 cm

### 3.6. Effect of Variation of EDTA Concentration

The effect of variation of EDTA concentration on the electrical output of cell has been studied having all factors common except EDTA concentration. Each cell has 30ml of solution including EDTA (different concentration in different cell), 3.8ml NaOH, 1.2 ml dye (Acid yellow-36) solution and double distilled water was taken as much to make total volume of solution equal to 30 ml.

A general increase in cell parameters like  $V_{OC}$ ,  $I_{SC}$ , and power was observed with increase in EDTA concentration up to  $7.33 \times 10^{-4}M$  and beyond this concentration, the decrease in the parameters has been found (Table 3). The reason for this observation may be that on the lower side of concentration range, there will be limited number of EDTA molecule to donate electrons to dye molecules therefore there is low electrical output or at higher concentration, EDTA molecule hindered the motion of oxidized reductant ( $EDTA^+$ ) molecule towards the electrode and hence there will be corresponding fall in power of the cell.

### 3.7. The effect of variation of light intensity on the electrical output of cell

The effect of variation of light intensity on the electrical output of cell has been studied having all factors common except light intensity. The intensity of incident light has been varied by using light source of different intensities (lamp of different wattages) and

results are reported in table 4. The photopotential and photocurrent increase with light intensity. The reason for this observation may be an increase in light intensity leading to a corresponding increase in the number of photons per unit area striking the dye molecules at the surface of the platinum electrode leading to, a raise in the output of the cell. At very high light intensity, the performance of the cell decrease for probable reasons (i) The dye molecules are limited in number, so large number of photons remains unutilized, (ii) there is less increase in power but high increase in intensity of light leads to lower efficiency as intensity is in denominator of formula of conversion efficiency and (iii) higher Intensity cause higher heating effect on the cell [13] leading to relatively poor performance of the cell.

### 3.8. Effect of variation of diffusion length

The effects of change in diffusion length ( $D_L$ ) *i.e.* distance between cathode and anode, on cell parameters have been studied having all factors constant except diffusion length. It is observed that with an increase in diffusion length, photopotential shows decrease and photocurrent shows increase (Table 5).

The photo potential decrease with diffusion length, the reason is that concentration gradient disturbs the photosensitizer layer on Pt electrode. As  $D_L$  increase the current increase as conductivity of dye increase due to increase in volume in solution between electrodes [11].

### 3.9. Effect of Variation of Electrode Area

The effect of variation of Pt electrode area on cell parameters has been studied having all factors common except electrode area. Under the observed effect of electrode area, the conversion efficiency and storage

capacity are found highest for electrode area  $0.25\text{cm}^2$ . The battery cell performance is found for small electrodes (table 5) owing to relatively less hindrance to diffusion of ions.

**Table 3: Effect of Variation of EDTA Concentration<sup>d</sup>**

[EDTA] $\times 10^{-4}$ M	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu\text{A}$ )	Power at power point( $\mu\text{W}$ )	Fill factor	Conversion efficiency (%)
6.00	649	200	51.76	0.39	1.99
6.66	666	213	61.30	0.43	2.35
7.33	685	230	71.50	0.45	2.75
8.00	670	216	62.52	0.43	2.40
8.66	648	207	52.45	0.39	2.02

<sup>d</sup>At  $\text{pH} = 11.65$ ,  $[\text{Acid Yellow-36}] = 4.00 \times 10^{-4}\text{M}$ ,  $\text{Temp} = 300\text{K}$ ,  $\text{Light intensity} = 10.4\text{mW cm}^{-2}$ ,  $\text{electrode area} = 0.25\text{cm}^2$ ,  $\text{Diffusion length} = 5.3\text{cm}$

**Table 4: Effect of variation of light intensity<sup>e</sup>**

Light intensity ( $\text{mW cm}^{-2}$ )	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu\text{A}$ )	Power at power point( $\mu\text{W}$ )	Fill factor	Conversion efficiency (%)
3.1	462	140	28.35	0.43	1.09
5.2	560	190	47.44	0.44	1.82
10.4	685	230	71.50	0.45	2.75
15.6	711	240	71.40	0.41	2.74
26	720	245	71.47	0.41	2.74

<sup>e</sup>At  $[\text{EDTA}] = 7.33 \times 10^{-4}\text{M}$ ,  $\text{pH} = 11.65$ ,  $[\text{Acid Yellow-36}] = 4.00 \times 10^{-4}\text{M}$ ,  $\text{Temp} = 300\text{K}$ ,  $\text{electrode area} = 0.25\text{cm}^2$ ,  $\text{Diffusion length} = 5.3\text{cm}$

**Table 5: Effect of Variation of Diffusion Length<sup>f</sup>**

Diffusion length (cm)	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu\text{A}$ )	Power at power point( $\mu\text{W}$ )	Fill factor	Conversion efficiency (%)
4.5	700	220	70.45	0.45	2.70
5.3	685	230	71.50	0.45	2.75
6.3	676	238	70.68	0.43	2.71
6.8	668	245	71.20	0.44	2.73

<sup>f</sup>At  $[\text{EDTA}] = 7.33 \times 10^{-4}\text{M}$ ,  $\text{pH} = 11.65$ ,  $[\text{Acid Yellow-36}] = 4.00 \times 10^{-4}\text{M}$ ,  $\text{Temp} = 300\text{K}$ ,  $\text{Light intensity} = 10.4\text{mW cm}^{-2}$ ,  $\text{electrode area} = 0.25\text{cm}^2$ .

**Table 6: Effect of Variation of Electrode Area<sup>g</sup>**

Electrode area ( $\text{cm}^2$ )	Photo-potential $V_{OC}$ (mV)	Photo-current $I_{SC}$ ( $\mu\text{A}$ )	Power at power point( $\mu\text{W}$ )	Fill factor	Conversion efficiency (%)
0.15	489	196	41.66	0.43	2.67
0.25	685	230	71.50	0.45	2.75
0.50	710	240	82.00	0.48	1.57
1.00	730	250	88.22	0.48	0.84

<sup>g</sup>At  $[\text{EDTA}] = 7.33 \times 10^{-4}\text{M}$ ,  $\text{pH} = 11.65$ ,  $[\text{Acid Yellow-36}] = 4.00 \times 10^{-4}\text{M}$ ,  $\text{Temp} = 300\text{K}$ ,  $\text{Light intensity} = 10.4\text{mW cm}^{-2}$ ,  $\text{Diffusion length} = 5.3\text{cm}$ .

#### 4. CONCLUSION

The photogalvanic cells have the promising conversion efficiency and storage capacity. In the present research work Acid yellow-36 dye has been used with EDTA and the observed conversion efficiency and storage capacity are 2.75 and 160 min. The earlier researchers did not observe the change in pH value of solution in cell, in present research work it is observed. The pH of solution continuously decreases during illumination of cell and become quite constant after some time.

For further improvement in performance of photogalvanic cell, the mixture of photosensitizers may be used which have broad absorption at different region of UV-Visible spectrum.

#### Conflict of interest

None declared

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