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Improved energy efficiency of photogalvanic cell with four dyes as photosensitizers in Tween 60- Ascorbic acid system

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The objective of this work was to increase the energy efficiency of photogalvanic cell using four dyes; Amido Black 10B, Bromocresol purple, Carmine and Biebrich scarlet as photosensitizers in Tween 60-Ascorbic acid system. Observed values of photopotential, photocurrent, fill factor, conversion efficiency and storage capacity for Tween 60 - Amido Black 10B - Ascorbic acid system were 996 mV, 420 µA, 0.38, 1.62%, 130 min, Tween 60 - Bromocresol purple - Ascorbic acid system were 811 mV, 65 µA, 0.50, 0.32%, 150 min, Tween 60 - Carmine - Ascorbic acid system were 844 mV, 190 µA, 0.43, 0.81%, 170 min. and Tween 60 - Biebrich Scarlet - Ascorbic acid system were 919mV, 210 µA, 0.41, 0.89%, 75 min, respectively. Comparative energy efficiency in all four systems studied in detail and all comparative data are discussed in the paper. Finally system with Amido black 10B and Carmine dyes was proposed as efficient system in view of solar energy conversion and storage.

Key words: Amido black 10B, bromocresol purple, carmine, biebrich scarlet, energy efficiency.

INTRODUCTION

Growing concern of rise in fossil fuel prices and environmental degradation has lead to the world's interest in renewable energy sources. Out of various renewable energy sources, solar energy is freely available and commercially viable source for electrical energy generation. The conversion of solar energy into electrical energy can be done by photoelectrochemical cells. The Photogalvanic effect was first reported by Rideal and Williams (1925) but it was systematically investigated by Rabinowitch (1940a, b). Later, various researchers reported this effect time to time (Kaneko and Yamada, 1977; Albery and Archer, 1977; Memming, 1980; Folcher and Paris, 1983; Pan et al., 1983; Naman and Karim, 1984; Jana, 2000; Ameta et al., 2006; Balzani et al., 2008; Ratcliff et al., 2011).

A new methodology of tilt angle for a solar panel to optimize solar energy extraction under cloudy conduction was reported by Armstrong and Hurley (2010). Photochemical energy conversion was studies in system containing methylene blue (Murthy and Reddy, 1979), analysis of galvano-statically synthesized polypyrole films, correlation of ionic difference and capacitance with the electrode morphology (Bisquert and Belmonte, 2002) and the molecular approaches to solar energy conversion and molecular control of interfacial charge transfer at nanocrystalline semiconductor interfaces (Meyer, 2005) were discussed.

Recently, studies on photogalvanic effect in mixed dyes and reductant systems were significantly reported (Yadav and Lal, 2010; Gangotri and Indora, 2010; Sharma et al., 2012). Some new dye-surfactant combination were studies in our laboratory in view of solar energy conversion and storage (Genwa and Kumar, 2012), but efforts are still needed to increase energy efficiency of

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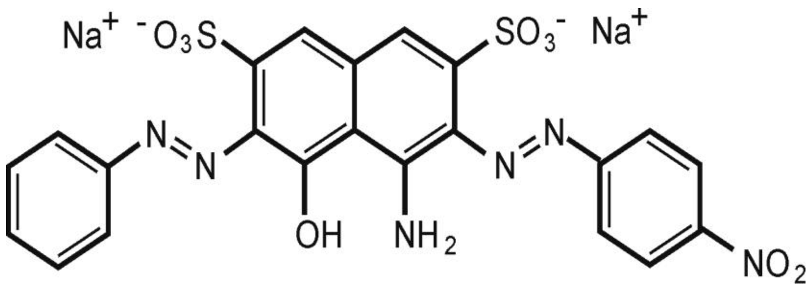
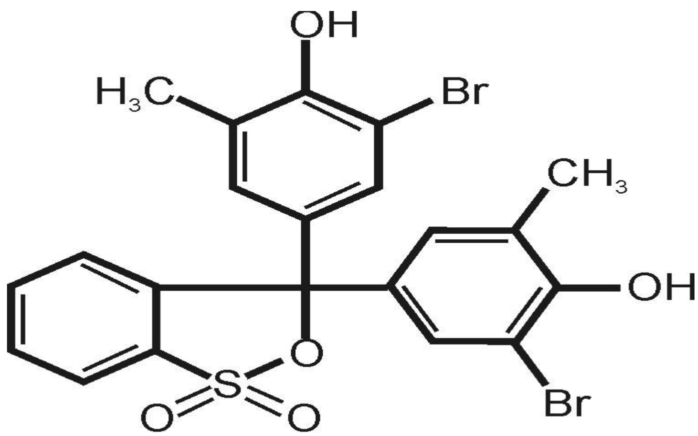


Scheme 1. Amido black 10B.



Scheme 2. Bromocresol purple.

photogalvanic cell. Therefore in this work, four dyes were selected and used as photosensitizer in photogalvanic cell to study comparative energy efficiency along with their storage performance.

MATERIALS AND METHODS

Amido black 10B

It was obtained from LOBA Chemie, Mumbai, India. Amido Black 10B (Scheme 1) is a solid crystalline black power, molecular formula $C_{22}H_{14}N_6Na_2O_9S_2$, molecular weight 616.49, soluble in water and maximum absorption (λ_{max}) 610 nm. Concentration of dye used cell solution was 1.1×10^{-5} M.

Bromocresol purple

It was obtained from LOBA Chemie, Mumbai, India. Bromocresol purple (Scheme 2) is a slightly yellow power, insoluble in water but soluble in Ethanol, molecular formula $C_{21}H_{16}Br_2O_5S$, molecular weight 540.24, and maximum absorption (λ_{max}) 580 nm . Concentration of dye used cell solution was 1.6×10^{-5} M.

Carmine

It was obtained from LOBA Chemie, Mumbai, India. Carmine (Scheme 3) is a solid red power, molecular formula is $C_{22}H_{20}O_{13}$, molecular weight is 492.39, soluble in water and maximum absorption (λ_{max}) 515 nm. Concentration of dye used cell solution was 7.2×10^{-5} M.

Biebrich scarlet

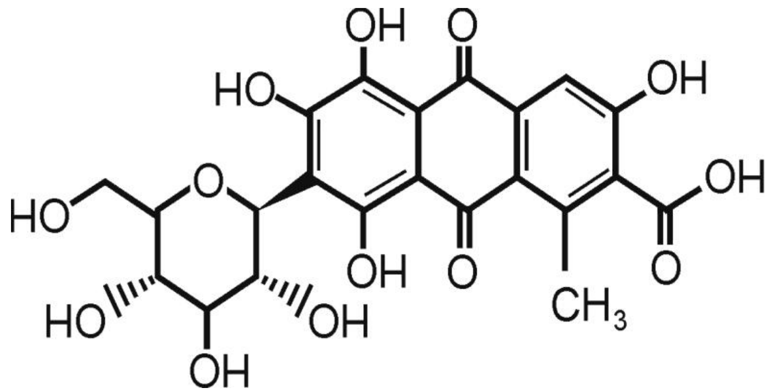
It was obtained from LOBA Chemie, Mumbai, India. Biebrich scarlet (Scheme 4) is dark red powder, soluble in water, molecular formula $C_{22}H_{14}N_4Na_2S_2$, molecular weight 556.9 and maximum absorption (λ_{max}) 520 nm. Concentration of dye used cell solution was 4.8×10^{-5} M.

Tween 60 (Polyoxyethylene sorbitan monostearate)

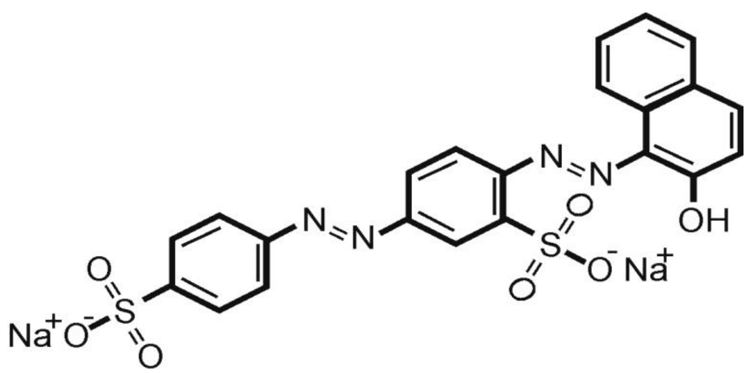
Tween 60 was obtained from LDH (Scheme 5) is a pale yellow semisolid liquid, soluble in water, molecular formula $C_{24}H_{46}O_6(C_2H_4O)_n$, molecular weight 1312. Concentration of Tween 60 used cell solution was 0.8 to 1.24×10^{-3} M.

Ascorbic acid

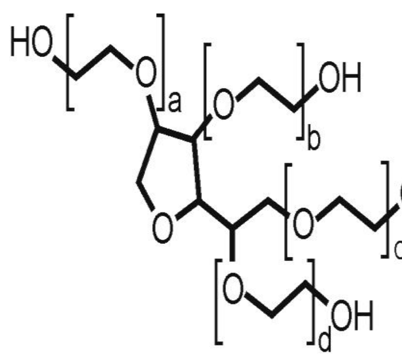
Ascorbic acid was used as reductant and it was obtained from SISCO, Mumbai, India (Scheme 6) is a white to slightly yellowish crystalline powder, soluble in water, molecular formula $C_6H_8O_6$ and molecular weight 176.13. Concentration of reductant used cell solution was 1.72 to 2.08×10^{-3} M.



Scheme 3. Carmine.

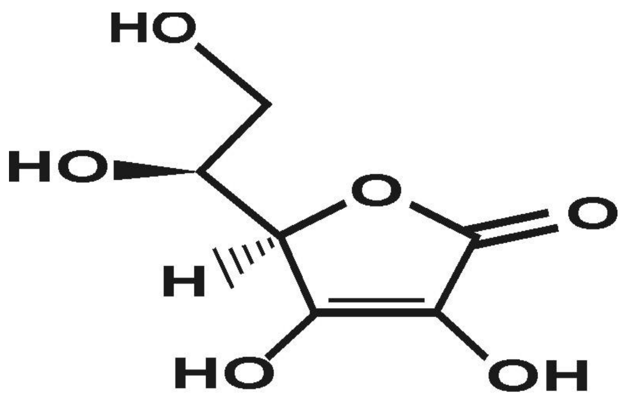


Scheme 4. Biebrich scarlet.



Scheme 5. Tween 60.

Photogalvanic effect of Tween 60 – Dye – Ascorbic acid systems was studied using H- shaped glass tube. Known amount of the solution of dye, reductant (ascorbic acid) and surfactant (Tween 60) was taken in the H-tube. NaOH was used to maintain the pH of solution in alkaline range. A platinum electrode ($1.0 \times 1.0\ cm^2$) was dipped in one limb and a saturated calomel electrode (SCE) immersed in another limb of the H- tube. The terminals of the electrodes were then connected to a digital pH meter (Systronics model 335, Ahmadabad, India). The entire system was first placed in dark until a stable potential was reached, then the limb containing platinum electrode was exposed to the light source (projector Tungsten lamp). The light intensity was varied by employing tungsten lamp of different wattage and measured by Solarimeter (Surya Systems, Ahmadabad). A water filter was placed between the illuminated chamber and the light source to cut off thermal radiations. The photochemical bleaching of dyes was studied potentiometrically. Absorption spectra of dye-surfactant combination have also been taken by using Spectrophotometer (Systronics 106, Ahmadabad, India) with the matched pair of silica cuvetts (path length 1 cm). All spectral measurements were



Scheme 6. Ascorbic acid.

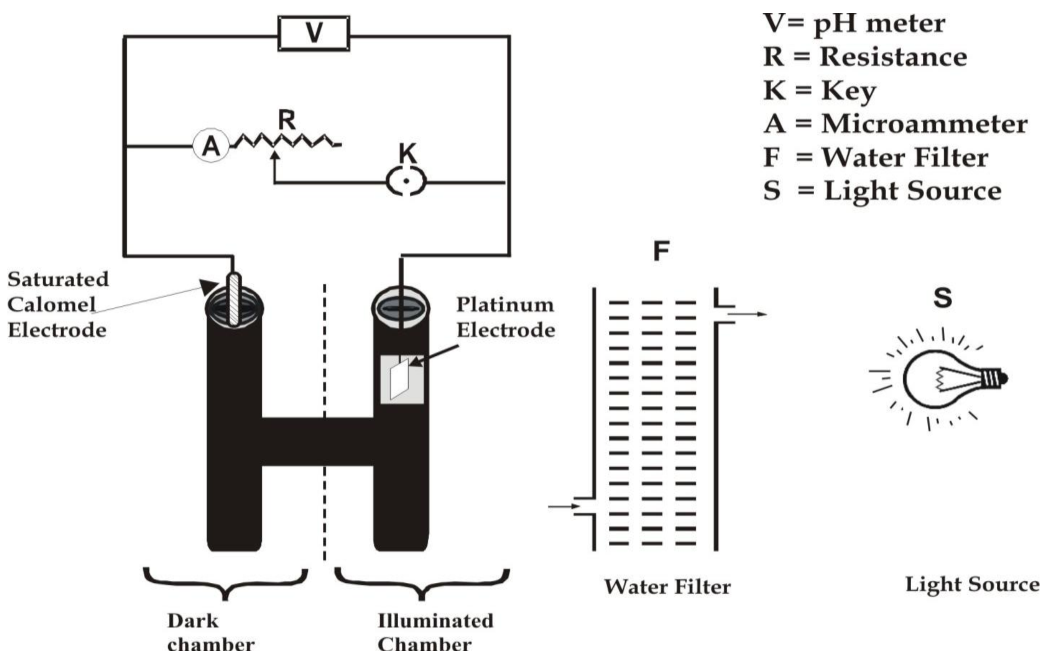


Figure 1. Set up of photogalvanic cell assembly.

duplicated in a constant temperature water bath maintained with in ±1°C and mean values were processed for data analysis. Over all experimental setup is shown in Figure 1.

RESULTS AND DISCUSSION

Effect of variation of pH

The pH of the cell solution affects the cell output in Tween 60 – Amido Black 10B – Ascorbic acid system, Tween 60 – Bromocresol purple – Ascorbic acid, Tween 60 – Carmine – Ascorbic acid and Tween 60 – Biebrich scarlet – Ascorbic acid systems. It was observed that there is an increase is in the photopotential and photocurrent with increase in pH and reaches maximum at pH 9.96 to 10.12, then on further increase in pH, photopotential and photocurrent decreased. It was further observed that these systems are sensitive to an alkaline medium and the pH for the optimum condition has a relation with pK_a of the reductant and desired pH is higher than its pK_a value ($pH>pK_a$). The reason may be the availability of reductant in its anionic form, which is better donor form. The pK_a value of ascorbic acid is 4.1 in experiment.

Effect of variation of surfactant (Tween 60) concentration

A nonionic surfactant Tween 60 was used in all four systems. It was found that electrical output of the cell increase on increasing the surfactant concentration

Table 1. Effect of variation of dyes concentration in Tween 60 – Dye – Ascorbic acid systems.

System	[Dye] $\times 10^{-5}$	Photopotential (mV)	Photocurrent (μA)
AB	0.3	794.0	295.0
	0.7	902.0	389.0
	1.1	996.0	420.0
	1.5	882.0	381.0
BCP	0.8	720.0	38.0
	1.2	768.0	53.0
	1.6	811.0	65.0
	2.0	763.0	54.0
	2.4	731.0	47.0
Carmine	6.4	816.0	104.0
	6.8	843.0	146.0
	7.2	884.0	190.0
	7.6	851.0	152.0
	8.0	825.0	118.0
BS	4.0	786.0	179.0
	4.4	856.0	194.0
	4.8	919.0	210.0
	5.2	836.0	182.0
	5.6	762.0	168.0

reaching a maximum value. On further increase in concentration of surfactant, a fall in electrical output was observed. The important properties of micellar systems are the ability to solubilize a variety of molecules and substantial catalytic effect on chemical reactions (Fendler and Fendler, 1975). The better electrical output of the photogalvanic cell was observed around the critical micelle concentration of the surfactant. The critical micelle concentration is the concentration of surfactant above which micelles form. The critical micelle concentration of Tween 60 is 0.22. Photoinduced electron transfer processes in micellar systems are potentially important for efficient energy conversion and storage, because surfactants help to achieve the separation of photoproducts by hydrophilic – hydrophobic interaction of the products with the micellar interface (Moroi et al., 1979). Thus, micelles not only solubilized the photosensitizer molecules to a maximum extent around their CMC values but have stabilized also the photogalvanic cell systems.

Effect of variation of photosensitizer concentration

The photogalvanic effect was studied in Amido Black 10B, Bromocresol purple, Carmine, Biebrich scarlet, photosensitizers in presence of Tween 60 and ascorbic acid in photogalvanic cell systems. It was observed that there was an increase in Photopotential (mV), photocurrent (μA) and power (μW) values on increasing the dye concentration (Table 1). A maxima was obtained for a particular value of photosensitizer concentration. On further increase in concentration of a photosensitizer, a decrease in the electrical output was observed. Low electrical output obtained in the lower concentration of photosensitizer due to limited number of photosensitizer molecules to absorb the major portion of the light in the path whereas a higher concentration of photosensitizer does not permit the desired light to reach the molecules near the electrodes and hence, corresponding fall in the electrical output of the cell was obtained.

Absorption properties of dye and dye + Tween 60

All dyes, Amido Black 10B, Bromocresol purple, Carmine and Biebrich scarlet were shown absorption in the visible region and different maximum absorption peak. It is clear from the absorption spectra of different dyes – surfactant combination that the concentration of surfactant shows a remarkable effect on absorbance of dye solution. On initial addition of surfactant solution (from 0.001 to 0.01%) to the dye solution, first a decrease in absorbance was observed. On further increasing the surfactant concentration an enhancement in absorbance was noticed at 0.05% concentration of surfactant (Figure 2a, b, c, d).

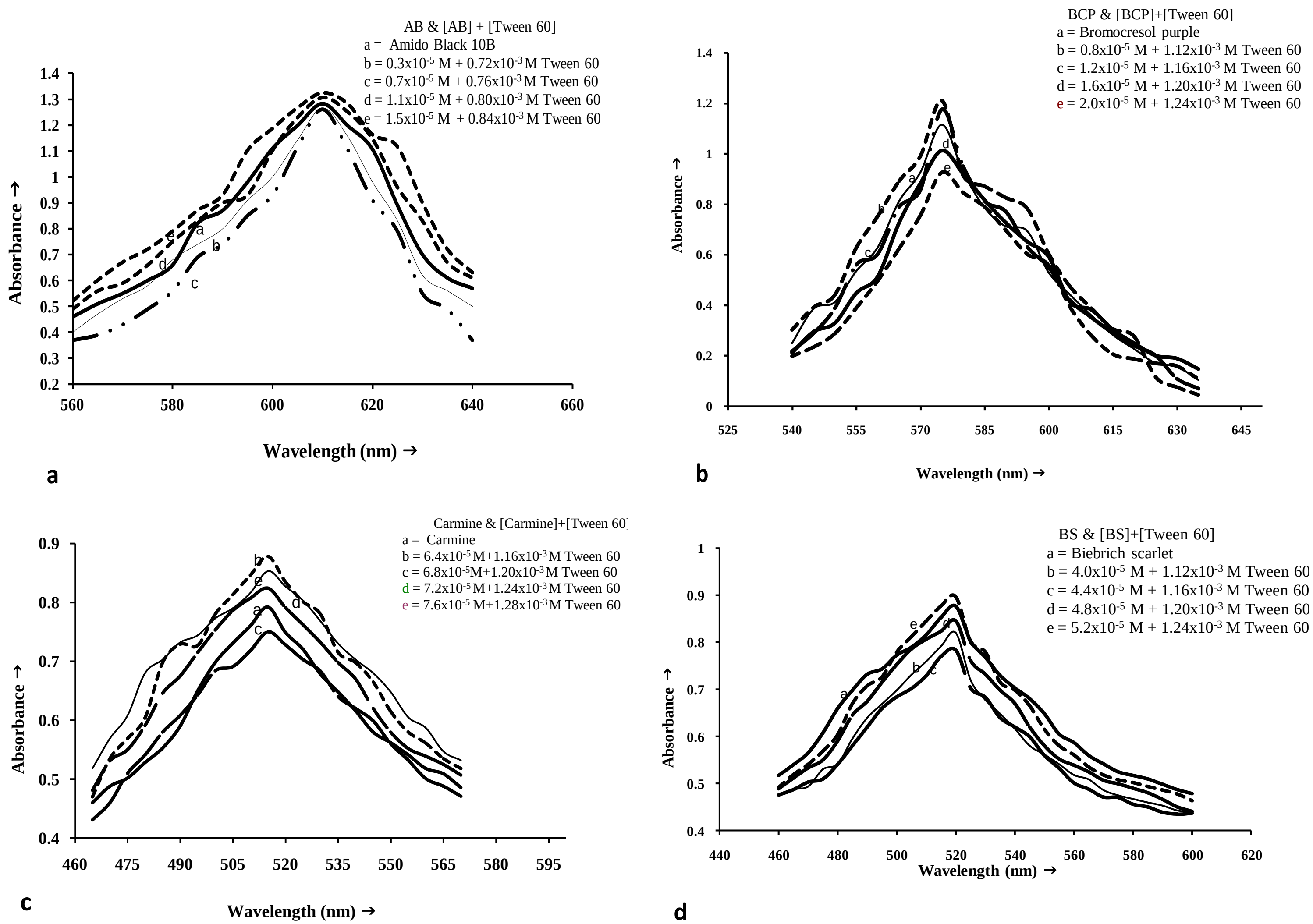


Figure 2. Absorption spectrum of dye and Dye + Surfactant (a) AB and AB- Ascorbic acid; (b) BCP and BCP- Ascorbic acid; (c) Carmine and Carmine- Ascorbic acid; (d) BS and BS- Ascorbic acid.

Effect of diffusion length

Effect of diffusion length on the electrical output (i_{max} and i_{eq}) and rate of initial generation of current (μA min^{-1}) of the photogalvanic cell were observed by using H-cell of different dimensions. The observed results are summarized in Table 2. It was observed that, i_{max} and rate of initial generation of current was found to increase

Table 2. Effect of diffusion length.

Diffusion length (D_L)	AB system	BCP system	Carmine system	BS system
Maximum photocurrent i_{max} (µA)				
50	477.0	117.0	198.0	191.0
55	489.0	124.0	228.0	212.0
60	500.0	130.0	250.0	235.0
65	511.0	135.0	281.0	258.0
70	522.0	140.0	308.0	280.0
Rate of initial generation of current (µA min^{-1})				
50	16.44	9.75	8.25	7.95
55	16.86	10.33	9.50	8.83
60	17.24	10.83	10.41	9.79
65	17.62	11.25	11.70	10.75
70	18.00	11.66	12.83	11.66

with diffusion length while i_{eq} shows a negligibly small decreasing behavior. The dye^- and dye are electroactive species in illuminated and dark chambers, respectively. In illuminated chamber dye^- strike at Pt electrode and donate electron to electrode which move through external circuit to reach calomel electrode (in dark chamber), electroactive species dye strike at calomel electrode and accept electron from it then through diffusion, dye^- reach to Pt and dye diffuse to dark chamber. Thus, the electrical output depends on diffusion and conductivity of dye. The conductivity of electro active spices depends on its population between electrodes. As the diffusion length is increased, the volume of photosensitizer solution and intern population of photosensitizer molecules increased leading higher i_{max}. The electro active nature of dye/ dye^- is proved by the fact that i_{max} increase with diffusion length. Therefore, it may be concluded that the main electro active spices are the leuco or semi form of dye^- and the dye in the illuminated and the dark chambers, respectively where as reductant and its oxidation products were act only as electron carries in the path.

Current– potential (i-V) characteristics of the cell

The short circuit current (i_{sc}) and open circuit voltage (V_{oc}) were measured with the help of a digital pH meter (keeping the circuit open) and from a microammeter (keeping the other circuit closed), respectively. The photocurrent and photopotential value in between these two extreme values were recorded with the help of a carbon pot (log 470K) connected in the circuit of the microammeter, through which an external load was applied. The corresponding values of potential with respect to different current values for Tween 60 – dye – Ascorbic acid systems are shown graphically in Figure 3a, b, c, d).

It was observed that the i-V curve deviated from its regular rectangular shapes in all four systems. A point in the i-V curve was determined where the product of current and potential was maximum called power point (pp), and their fill factor values have also been calculated. Some important i-V characteristics of four systems are given in Table 3. On the basis of these comparative data, the order of efficiency of photogalvanic cells on the basis calculated fill factor is: Tween 60 – Bromocresol purple – Ascorbic acid system > Tween 60 – Carmine – Ascorbic acid system > Tween 60 – Biebrich scarlet – Ascorbic acid system > Tween 60 – Amido black 10B – Ascorbic acid system.

Performance (storage capacity) of the cell

The performance or storage capacity of the photogalvanic cells containing four different systems were studied by applying an external load log 470K (necessary to have current at power point) reaches after removing the source of illumination. It was quite interesting observed that the performance of the cell dark was affected appreciably in the presence of various dyes. The performance was determined in terms of $t_{1/2}$, that is, the time required in fall of the power output to its half at power point in dark. Comparative values of power and $t_{1/2}$ of all four systems are given in Table 4 and graphically represented Figure 4.

On this basis of above observations, the order of performance of these cells in dark on the basis of $t_{1/2}$ is as follows: Tween 60 – Carmine – Ascorbic acid system > Tween 60 – Bromocresol purple – Ascorbic acid system > Tween 60 – Amido black 10B – Ascorbic acid system > Tween 60 – Biebrich scarlet – Ascorbic acid system.

Conversion energy efficiency of the cell

Conversion efficiency of all four photogalvanic systems

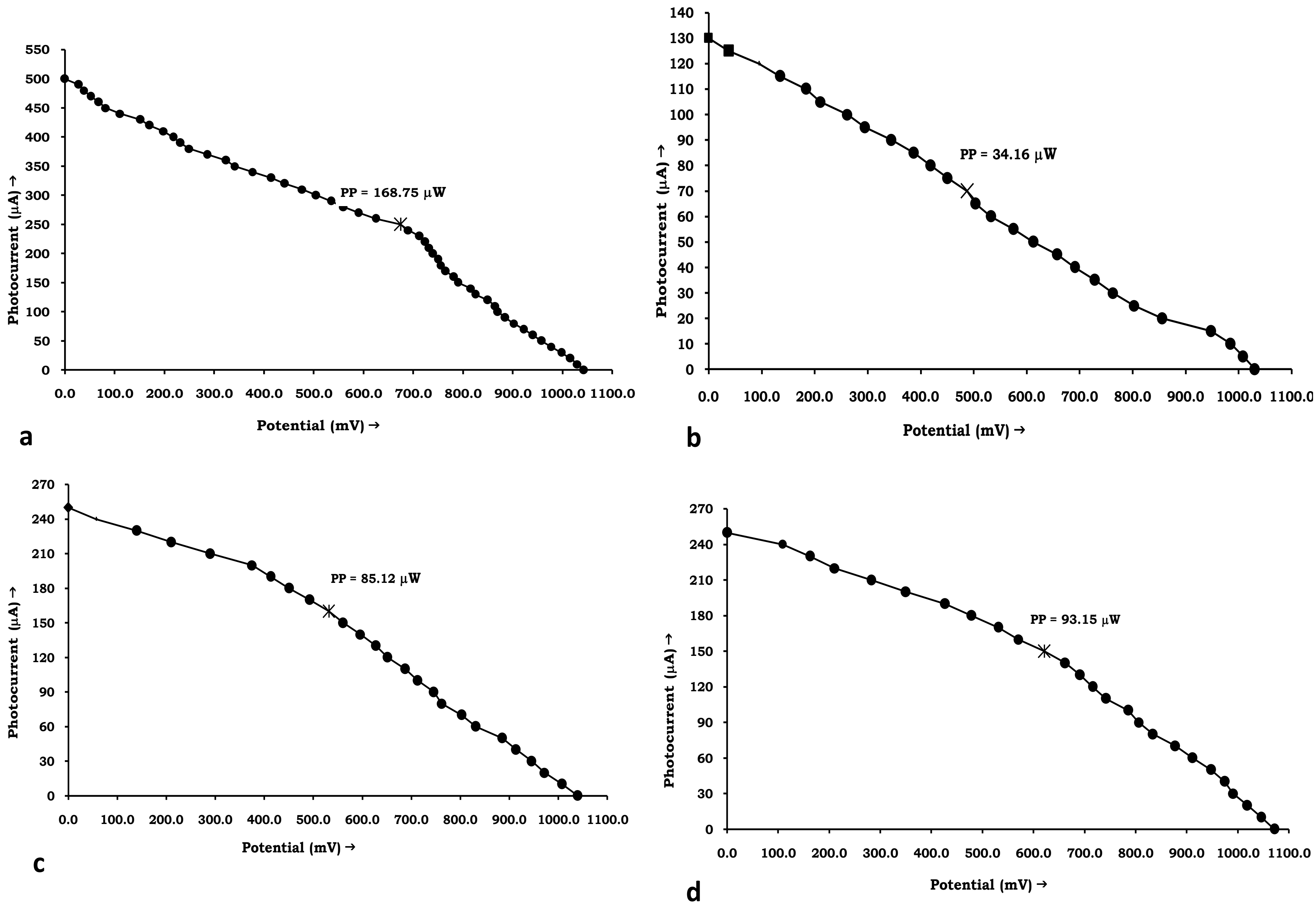


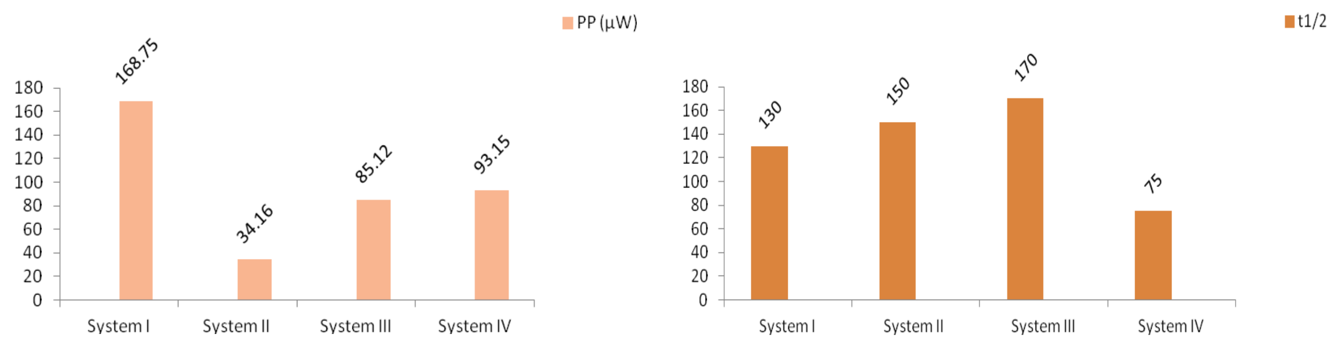
Figure 3. Current – potential (i-V) curve of the cell Surfactant (a) AB- Ascorbic acid; (b) BCP- Ascorbic acid; (c) Carmine- Ascorbic acid; (d) BS- Ascorbic acid system.

Table 3. Current– Potential (i-V) characteristics of the cell.

System	V_{oc} (mV)	i_{sc} (μA)	V_{pp} (mV)	i_{pp} (μA)	Fill factor (*ff*)
Tween 60 – AB – Ascorbic acid	1043	420	675	675	0.38
Tween 60 – BCP – Ascorbic acid	1031	65	488	70	0.50
Tween 60 – Carmine – Ascorbic acid	1040	190	532	160	0.43
Tween 60 – BS – Ascorbic acid	1072	210	621	150	0.41

Table 4. Performance of the photogalvanic cells in dark, conversion energy efficiency and sunlight conversion data.

System	Power (PP) (μW)	$t_{1/2}$ (Min.)	Conversion efficiency η (%)	Sunlight conversion data	
				Potential (mV)	Current (μA)
Tween 60–AB–Ascorbic acid	168.75	130	1.6226	2988	1260
Tween 60–BCP–Ascorbic acid	34.16	150	0.3284	2433	195
Tween 6–Carmine–Ascorbic acid	85.12	170	0.8184	2652	570
Tween 6 –BS–Ascorbic acid	93.15	75	0.8960	2757	630



(a) (b)

Figure 4. (a) Power and (b) Storage capacities of cell systems.

were calculated with the help of current and potential values at power point (PP) and the incident power of radiations, the conversion efficiency of the cell was determined (Equation 1). The observed values of conversion efficiencies are better than previously reported studies (Gangotri and Gangotri, 2010). The conversion energy efficiency and sunlight conversion data of all four systems are summarized in Table 4 and graphically in Figure 5. On the basis of these observations, photogalvanic cell containing four different dyes systems, the order on the basis of conversion efficiency is: Tween 60 – Amido black 10B – Ascorbic acid system > Tween 60 – Biebrich scarlet – Ascorbic acid system > Tween 60 – Carmine – Ascorbic acid system > Tween 60 – Bromocresol purple – Ascorbic acid system.

$$\text{Conversion efficiency } (\eta) = \frac{V_{pp} \times i_{pp}}{} \times 100\% \quad (1)$$

Mechanism

On the basis of above observations and discussion, the mechanism for generation of electrical output in the photogalvanic cell may be proposed as follow:

Illuminated chamber

On irradiation, dye molecule get excited

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^* \quad (2)$$

The excited dye molecules accept an electron from reductant and convert into semi or leuco form of dye, and the reductant into its excited state form:

$$\text{Dye}^* + \text{R} \longrightarrow \text{Dye}^-(\text{semi or leuco}) + \text{R}^+ \quad (3)$$

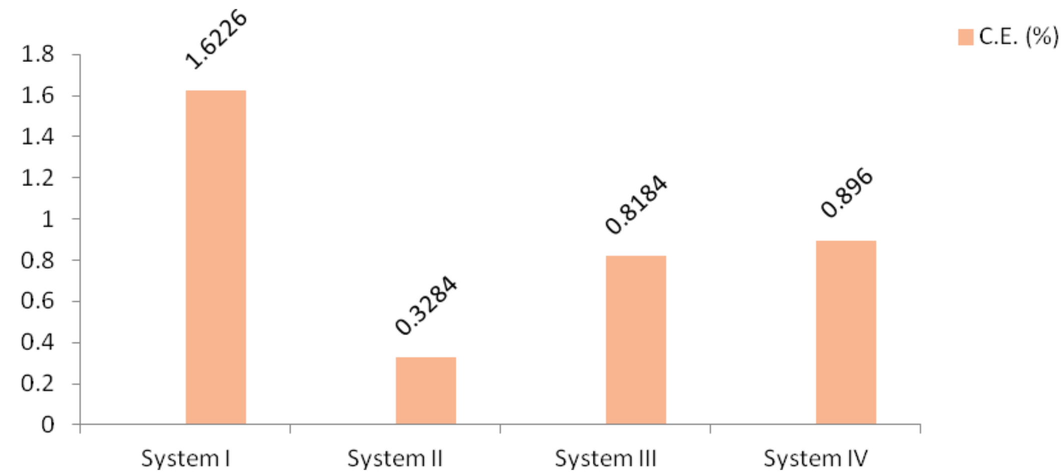


Figure 5. Conversion efficiencies of cell systems.

At platinum electrode: The semi or leuco form of dye loses an electron and converted into original dye molecule.

$$Dye^{-} \longrightarrow Dye + e^{-} \quad (4)$$

Dark chamber

At counter electrode

$$Dye + e^{-} \longrightarrow Dye^{-}\ (\text{semi or leuco}) \quad (5)$$

Finally, leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule and the cycle will go on:

$$Dye^{-} + R^{+} \longrightarrow Dye + R \quad (6)$$

Where, Dye, Dye*, Dye^{-}, R and R^{+} represents the dye, excited form, reduced of dye, reductant and oxidized form of reductant, respectively.

Conclusions

The photogalvanic cells have inbuilt power storage capacity which can be used in absence of sunshine hours (no need of any hardware like batteries). Present work is a successful effort to conversion of solar energy into electrical energy by photogalvanic conversion technology.

Four different dyes (Amido Black 10B, Bromocresol purple, Carmine and Biebrich scarlet) were used as photosensitizers along with a surfactant Tween 60 and Ascorbic acid as a reductant in this work. In all photogalvanic cell systems, possible variations of all parameters are experimentally observed. The fill factor conversion efficiency, power of storage capacity of all systems was determined. On the basis of these results, conversion efficiency point of view Tween 60 – Amido black 10B – Ascorbic acid system is a most efficient followed by Tween 60 – Biebrich scarlet – Ascorbic acid system, Tween 60 – Carmine – Ascorbic acid system and Tween 60 – Bromocresol purple – Ascorbic acid system. Storage capacity point of view Tween 60 – Carmine – Ascorbic acid system is a most efficient followed by Tween 60 – Bromocresol purple – Ascorbic acid system, Tween 60 – Amido black 10B – Ascorbic acid system and Tween 60 – Biebrich scarlet – Ascorbic acid system.

Finally, it may be concluded that Amido black 10B and Carmine dyes are efficient to be used in photogalvanic cell for conversion efficiency and storage capacity and in view of generation of electrical out-put. In future, efforts will be made to enhance these two factors along with their practical/field implementation.

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Nomenclature: $\mathbf{V_{oc}}$**,** Open circuit voltage; **ΔV,** photopotential; $\mathbf{i_{max}}$**,** maximum photocurrent; $\mathbf{i_{eq}}$**,** equilibrium photocurrent; $\mathbf{i_{sc}}$**,** short circuit current; $\mathbf{i_{pp}}$**,** current at power point; $\mathbf{V_{pp}}$**,** potential at power point; ***f f*,** fill factor; **η,** conversion efficiency; $\mathbf{D_L}$**,** diffusion length; **A,** electrode area; **PS,** photosensitizer; **AB,** amido black 10B; **BCP,** bromocresol purple; **BS,** biebrich scarlet.

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