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## **Photogalvanic cells: Comparative study of various synthetic dye and natural photo sensitizer present in spinach extract**

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### **Abstract**

The photogalvanic cells (PG) are dye sensitized solution phase based solar power generation and storage devices. The photogalvanics of various synthetic dyes (single/mixed) and natural photo sensitizers (present in crude spinach extract) has been studied to have some new insights with aim of finding relatively cheaper, cleaner and nature friendly photo sensitizers for further improvement in electrical performance of PG cells. In this study, at illumination intensity  $10.4 \text{ mWcm}^{-2}$ , the observed value of electrical output for single as well as mixed photo sensitizers is of the same order, and surprisingly very high with respect to earlier reported results. Therefore, it may be concluded that mixed photo sensitizers does not offer any significant advantage over single photo sensitizers. Therefore, I suggest focus on single photo sensitizers, and more on natural photo sensitizers like chlorophyll present in crude spinach extract for cost-effective, eco-friendly and renewable cells.

**Key Words:** Photogalvanic cell, solar energy, Storage capacity, Spinach extract.

### **1. Introduction**

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Like dye-sensitized<sup>1</sup> and plastic solar cells<sup>2</sup>, the photogalvanic cell technique provides a promising and unexplored method for solar power generation and storage. The photogalvanic cell is a device involving ions as mobile charges moving in solution through diffusion process. The sensitizer in solution is photoexcited (energy rich product), which in turn can lose energy electrochemically to generate electricity with inherent storage capacity.

The photogalvanic effect was observed during the action of light on the ferrous iodine-iodide equilibrium<sup>3</sup>. Rabinowitch suggested that the photogalvanic effect might be used to convert sunlight into electricity<sup>4</sup>. To explore this suggestion, some photogalvanic cells using the iron-thionine system as the photosensitive fluid were tested<sup>5</sup>. The observed maximum power conversion efficiency was  $3 \times 10^{-4}$  per cent. The principal reason for the low efficiency was shown to be polarization of the polished platinum electrodes and rapid loss of the photochemical activity of the dye. Coating the electrodes with platinum black reduced polarization sufficiently. In principle, it appeared possible to make further increases in efficiency by increasing electrode area and decreasing the electrolyte resistance. The maximum power conversion efficiency that could be achieved from a photogalvanic cell is between 5 and 9 %. The power conversion efficiency of the optimal cell could be as large as 18 % but it is unlikely that all the necessary conditions can be met<sup>6</sup>, and a sufficient range of the solar spectrum can be used<sup>7</sup>.

Photogalvanic cells based on Chlorophyll-a (Chl-a) plated Pt electrode and Chl-a free Pt electrode<sup>8</sup>, various inorganic compounds<sup>9-12</sup>, micro-emulsions with micellar solution<sup>13</sup>, and various organic dye photosensitizers with organic reductants and surfactants<sup>14-26</sup> in doubly distilled water have been studied. In beginning, photogalvanics emphasized the

importance of coated Pt electrode with  $\text{Fe}^{2+}$  as reducing agent. Later on, the researcher started using non-coated Pt electrode with saturated calomel electrode.

The literature reveals lack of reports focusing on use of (1) mixture of the photosensitizers having absorption maxima in different part of solar spectrum, (2) natural photosensitizers in free State in crude spinach extract, and (3) singly distilled water in photogalvanic cells. The reported electrical parameters of photogalvanic cells are also low. So, the use of suitable photosensitizers with reductant in photogalvanic cells is needed for higher electrical output. Towards this direction, the study of photogalvanics of various single and mixed photosensitizers with Fructose as reductant, Sodium Lauryl Sulphate (NaLS) as surfactant, saturated calomel electrode (of combination electrode) and Pt electrode of very small area was undertaken.

The most convenient spectral region for use in solar energy conversion and storage is 400 nm-800 nm. Earlier researchers in the field of photogalvanics used single or mixed photosensitizers having absorption maxima in a particular region of 400 nm-800 nm.

The reported work in photogalvanics shows study of single dyes mostly having absorption near 600 nm<sup>20, 27</sup>. The use of mixed dyes [methylene blue ( $\lambda_{\text{max}}$  665 nm) + thionine ( $\lambda_{\text{max}}$  598 nm)]<sup>28</sup> will also not be able to use much broader spectrum. Therefore, the earlier work could use only narrow spectrum for solar energy conversion and storage. The failure to use broader solar spectrum was cited as one of the reason for lower performance of the photogalvanic cells<sup>7</sup>. The study of photogalvanics of various dyes and natural photo sensitizers (present in spinach extract) was, therefore, undertaken to have some new insights with aim of finding relatively more cheap, clean and nature friendly photo sensitizers for further improvement in electrical performance of these cells.

Therefore, the present research work was undertaken to enhance the electrical output of cells and to see whether (1) use of mixture of the photosensitizers having absorption maxima in different parts of solar spectrum could result in enhancement of electrical performance of photogalvanic cells, (2) we should use single photosensitizer or mixture of the photosensitizers having absorption maxima in different parts of solar spectrum, (3) the use of natural photosensitizers present in crude spinach extract may result in electrical output as that for synthetic dye photosensitizers, and (4) the use of singly distilled water may result in electrical output as that for doubly distilled water. For this, photosensitizers (Sudan-I,  $\lambda_{\max}$  476 nm; Rhodamine-B,  $\lambda_{\max}$  543 nm; Fast Green FCF,  $\lambda_{\max}$  622-626 nm; Brilliant Cresyl Blue,  $\lambda_{\max}$  622 nm; Spinach extract (Chlorophyll a & b),  $\lambda_{\max}$  435 & 680 nm; Naphthol Green B,  $\lambda_{\max}$  714 nm) having absorption maxima in different regions of 400 nm-800 nm have been used. The Fructose was chosen as reducing agent due to its widely known good reducing property in rapid Furfural test. The crude spinach extract have been used to make photogalvanic cells more eco-friendly and renewable energy sources as these cells have used so far synthetic dye photosensitizer(s) only.

## 2. Results and discussion

### 2.1. Mechanism of photocurrent generation and storage capacity

The photogeneration of current involves the photo-excitation of sensitizer molecules to form their singlet excited state and through inter-system crossing the triplet excited state. In a system of large number of particles as in present study, the spontaneous decay of excited states to the ground state follows first order kinetics. The lifetime of singlet and triplet state is of the order of  $10^{-9}$ - $10^{-7}$  sec and  $10^{-4}$  sec-10 sec, respectively<sup>29</sup>. These excited sensitizer molecules takes electron from the reductant fructose to form the

reduced semi or leuco forms. These reduced forms of the sensitizer molecules having excess electrons undergoes oxidation by transferring their excess electron to the Pt electrode (Illuminated Chamber-anode) leading to generation of the current. At SCE (Dark Chamber-cathode), the dye molecule accepts an electron from electrode and gets converted into semi or leuco form. Finally, leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecules<sup>14</sup>. This cycle goes on in cell (**Fig.S1**).

## 2.2. Variation of the photopotential with time during charging of the cells

The photogalvanic effect of single and mixture of photosensitizers has been studied by constructing fifteen photogalvanic cells having all factors common except photosensitizer(s) and their concentrations. Each cell has total 25 mL solution including photosensitizer(s), Fructose, NaOH, NaLS and single distilled water (**Table 1, See 1.2 of SI**).

Detailed dimensions of the each photogalvanic cells are as Pt electrode area  $0.4 \times 0.2 \text{ cm}^2$ , saturated calomel electrode (SCE) of combination electrode as counter electrode, Diffusion Length ( $D_L$ ) 5.6 cm, and artificial illumination intensity  $10.4 \text{ mW cm}^{-2}$ . Each cell contained total 25 ml solution mixture [1.6 ml of M/100 Fructose (resultant concentration  $6.4 \times 10^{-4} \text{ M}$ ); 1.0 ml of M/10 NaLS (resultant concentration  $4.0 \times 10^{-3} \text{ M}$ ); 3.6 mL of 1M NaOH (resultant pH 13.15) for cell no.1 to 10 and 7.0 mL of 1M NaOH (resultant pH 13.44) for cell no.11 to 15; and dye(s)/sensitizer(s) solutions as in **Table 1**]. The various cells constructed were charged in artificial sunlight ( $10.4 \text{ mW cm}^{-2}$ ). On illumination of photogalvanic cells, the potential increases regularly and reaches to a highest value ( $V_{\text{max}}$ ), which then decreases and becomes quite constant ( $V_{\text{oc}}$ ) after some time [**Table S1, Fig.1, Fig.S2 (a, b, c, d)**]. Under the conditions of observation and

taking technical and manual errors into account, the pattern of change of photopotential with time and value of the  $V_{\max}$  and  $V_{oc}$  is more or less same for all systems [Fig.1, Fig.S2 (a, b, c, d)]. From these observations, we may infer that mixing of photosensitizers having  $\lambda_{\max}$  in different regions of solar spectrum does not affect the photopotential and its variation with time during illumination of the cells.

### 2.3. Variation of the potential and power with current (i-V characteristics)

The i-V characteristics show that potential varies inversely with current for all cells, and the pattern of change of potential with current is similar for all cells [(Fig.S3 (a, b, c, d)]. From these observations, we may infer that mixing of photosensitizers having  $\lambda_{\max}$  in different regions of solar spectrum does not affect the change of potential with current.

### 2.4. Change of power with time (Study of cell performance at $P_{pp}$ )

The i-V characteristics show that highest power (i.e., power at power point- $P_{pp}$ ) is extractable from various cells at a certain current and resistance. The values of current and resistance at which highest power is extractable from various cells is different (but only slightly) for different cells [Fig.2 (a, b)]. Therefore, the cell performance of various cells in dark has been studied at respective currents and resistances at which their power is highest.

The current, potential and power decreases with time [Table S2, Fig.3, Fig. S4 (a, b, c)]. This is because the number of available sensitizer molecules in reduced form undergoing oxidation at Pt electrode decreases with time. The power at power point reduces to its half value in half change time ( $t_{0.5}$ ). Even after the  $t_{0.5}$ , the cell continuously supplies power until complete discharge. The cells do not have unlimited life as the lifetime of the excited state of any sensitizer molecule is not infinity and, therefore, the sensitizer molecules in reduced form are not available for infinity time in the dark.

## 2.5. Discussion of results of various single photosensitizers

The electrical cell parameters for various individual and mixed photosensitizers are summarized in **Table 2** and **Fig. S5 (a, b)**.

The value of  $P_{pp}$  for various single photosensitizers that are Naphthol Green B (NGB), Fast Green FCF (FCF), Brilliant Cresyl Blue (BCB), Spinach extract (SPE), Rhodamine-B (RHD) and Sudan (SUD) is 204.1  $\mu\text{W}$ , 186  $\mu\text{W}$ , 216.9  $\mu\text{W}$ , 264  $\mu\text{W}$ , 272.4  $\mu\text{W}$ , and 316.8  $\mu\text{W}$ , respectively [**Table 2, Fig. S5 (a)**]. The value of  $P_{pp}$  is slightly different for different single photosensitizers. Under the observed conditions, the SUD ( $\lambda_{\text{max}}$  476 nm) has highest power output. The reason may be that lower m.w. (i.e., 248.28) of SUD enables it to diffuse more in solution inside cell leading to higher current and electrical output as Photogalvanic cell is diffusion controlled. The molecular weights of other photosensitizers is 479.02 (RHD), 808.84 (FCF), 385.96 (BCB), 878.46 (NGB), and Chlorophyll-a (893.52) & Chlorophyll-b (907.51) present in SPE. The power for RHD is slightly less than that for SUD as the m.w. of RHD is slightly higher than that for SUD. The power for other single photosensitizers is of the same order as their m.w. is of the same order. Given the structure of BCB [**Fig.S6 (a, b)**], the effective m.w. for it may be of the order of 516. The photogalvanics of all cells having single photosensitizers has been studied at equimolar concentrations of all chemicals including photosensitizer, Fructose, NaLS and NaOH. Thus, we may conclude that photosensitizer of m.w. of the same order shows more or less same electrical performance under equimolar conditions with taking errors in to consideration. Therefore, photogalvanics based on single photosensitizers must focus on cheap and eco-friendly photosensitizers. The use of SUD gives relatively higher power out put. Despite it, its use is not advisable as it is synthetic and water insoluble (soluble in alcohol). Therefore, use of SUD in photogalvanics will



not be cost-effective, renewable and eco-friendly. Taking in to account the economic and environmental cost of SUD, the power out put of SUD based cells is disadvantageous.

## 2.6. Discussion of results of various mixed photosensitizers

First of all, a cell based on single photosensitizer NGB ( $\lambda_{\max}$  714 nm) was studied. Photogalvanics of mixed photosensitizers was studied with respect to performance of the single photosensitizer NGB based cell. Photogalvanics of mixed photosensitizers was studied in two ways.

One, the concentrations of reductant, surfactant and NaOH was kept constant, and mixing of individual photosensitizers was done by taking concentration of individual photosensitizers equal to concentration of NGB taken in cell based on single photosensitizer NGB.

A cell (cell no.1) based on single photosensitizer NGB ( $\lambda_{\max}$  714 nm) was studied using 0.38 ml M/500 NGB, 1.0 ml M/10 NaLS, 3.6 ml 1M NaOH, 1.6 ml M/100 Fructose and rest single distilled water to make total volume of solution 25 ml. The observed  $P_{pp}$  was 204.1  $\mu$ W. The NGB based cell is thought to use narrow spectrum (i.e., radiations near 714 nm) for solar energy conversion and storage.

For study of mixed photosensitizers, four cells were fabricated (cell no. 7, 8, 9, 10; Table 1).

The NGB (714 nm) + FCF (622 nm) based Photogalvanic cell no.7 was studied for using relatively broader spectrum (i.e., radiations ranging from 800-700 to 700-600 nm) for solar power generation. The NGB (714 nm) + FCF (622 nm) + RHD (543 nm) based photogalvanic cell no.9 was studied for using relatively broader solar spectrum (i.e., radiations ranging from 800-700 to 700-600 to 600-500 nm). The cell no. 10 based on NGB (714 nm) + FCF (622 nm) + BCB (622 nm) + SPE (435 nm & 680 nm) + RHD

(543 nm) + SUD (476 nm) was studied for using almost whole visible region (i.e., 800-700 to 700-600 to 600-500 to 500-400 nm) for solar energy conversion and storage.

If we compare results of mixed photosensitizer based cell no. 7 to 10, the power output is more or less same, although broader solar spectrum is being used going from cell no. 7 to 10 [**Table 2, Fig. S5 (a)**]. Further, if we compare results of mixed photosensitizer based cell no.7 to 10 with that of single photosensitizer NGB based cell, we find that power output of mixed photosensitizers is only slightly greater than that of single photosensitizer.

Two, the concentrations of reductant, surfactant and NaOH was kept constant, and mixing of individual photosensitizers was done by taking such concentration of individual photosensitizers so as to keep total concentration of mixed photosensitizers equal to concentration of NGB taken in cell based on single photosensitizer NGB.

A cell (cell no.11) based on single photosensitizer NGB ( $\lambda_{\max}$  714 nm) was studied using 0.38 ml M/500 NGB, 1.0 ml M/10 NaLS, 7.0 ml 1M NaOH, 1.6 ml M/100 Fructose and rest single distilled water to make total volume of solution 25 ml. The observed  $P_{pp}$  was 422.4  $\mu$ W. The NGB (714 nm) based cell is thought to use narrow spectrum (i.e., radiations near 714 nm) for solar energy conversion and storage.

For study of mixed photosensitizers, four more cells were fabricated (cell no. 12, 13, 14, 15; **Table1**).

The NGB (714 nm) + FCF (622 nm) +BCB (622 nm) based Photogalvanic cell no.12 was studied for using relatively broader spectrum (i.e., radiations ranging from 800-700 to 700-600 nm) for solar power generation. Similarly, cell no.13 and 14 were studied for using relatively broader spectrum. The cell no. 15 based on NGB (714 nm) + FCF (622

nm) + BCB (622 nm) + SPE (435 nm & 680 nm) + RHD (543 nm) + SUD (476 nm) was studied for using almost whole visible region (i.e., 800-700 to 700-600 to 600-500 to 500-400 nm) for solar energy conversion and storage.

If we compare results of various mixed photosensitizer based cell no. 12 to 15, the power output is more or less same, although broader solar spectrum is being used going from cell no. 12 to 15 [Table 2, Fig. S5(b)]. Further, if we compare results of mixed photosensitizer based cell no.12 to 15 with that of single photosensitizer NGB based cell no. 11, we find that power output of mixed photosensitizers is more or less equal to that for single photosensitizer.

According to the mechanism of photogeneration of current in photogalvanic cells and sensitization concept, the current and conversion efficiency will be dye-dependent. And, it has also been observed in present work, but this dependence does not appear to have significant effect on cell performance (Table 2). The  $V_{oc}$  and  $i_{sc}$  is slightly different for different single and mixed dyes in line with slightly different redox potentials of different dyes. The reason for similarity of output for single and mixed sensitizers may be as follows-

- (a) for each sensitizer(s), the value of various cell fabrication parameters (like Pt, SCE, pH, NaLS conc., illumination intensity, diffusion length, dilution, dye conc., etc.) is similar. So in similar conditions, output is quite similar.
- (b) The current generation depends on particle nature (number of electrons), and light intensity and concentration is also of particle nature.

The equimolar NaLS solutions will have equal number of NaLS molecules. Similarly, equimolar dye(s) solutions will have equal number of dye molecules as dye solution is very dilute. So very dilute nature of dye solutions in presence of solubilizing agent NaLS is expected to show similar dye solubility in case of each single dye and mixed dye sensitizers. Thus, in each case, the number of molecules of chemicals and photons are the same to give and take nearly same number of electrons.

The illumination intensity used is  $10.4 \text{ mWcm}^{-2}$ . About 44 % of this consists of visible spectrum. At this intensity, considering average wavelength 550 nm of visible range, the photon intensity of the order of  $1.25 \times 10^{16} \text{ photons s}^{-1} \text{cm}^{-2}$  is striking the solution inside the cell. Whether 90 % or 10 % of this intensity is absorbed by single/mixed dyes as their absorbance is different, then for each single or mixed dye system the number of photons absorbed will be of the order of  $10^{16} \text{ photons s}^{-1} \text{cm}^{-2}$ . Thus, for all single and mixed dye systems, the number of absorbed photons will be nearly same, and therefore, electron ejection (Internal Quantum Efficiency -IQE) in all cases will also be of same order. For electrical output, electrons are needed. At which wavelength (715 nm or 622 nm or others), the electrons from photosensitizer are ejected does not affect the cell output. Number of electrons emitted from sensitizer is more important. Number of electrons emitted from equimolar solution of photosensitizers is expected to be nearly same and independent of the  $\lambda_{\text{max}}$  under identical conditions of cell dimension, concentration and illumination as number of dye molecules, number of photons illuminating, and redox potential (potential governs the electron donation/acceptor capacity of sensitizers) is nearly same. To be noted that redox potential of dyes is pH dependant<sup>30</sup>, and is found to have positive relation with pH at high pH range. Therefore, the redox potentials of all

dyes in present work may be of the same order as pH used is of highest range (i.e., ~13)<sup>30</sup>.

The charging time for each cell is short. This short time may be the reason for higher efficiency as long sensitization time results in decreased solar cell efficiency because of decreased efficiency of electron injection<sup>31</sup>. Therefore, in present study, the similarity of efficiency in each cell may also be due to the fact that charging time for cells based on all single and mixed dyes is of the same order.

Thus, by taking errors in to consideration, it may be concluded that (i) single photosensitizers have electrical output of the same order, (ii) all kinds of mixing of photosensitizers has electrical output of the same order, (iii) the mixed photosensitizers shows more or less same electrical performance as for single sensitizers, and (iv) natural resources like crude spinach extract shows same performance as shown by synthetic sensitizers. It means the photogalvanics of mixed photosensitizer does not offer any significant advantages over single photosensitizers, and these cells can be used with same efficiency in all parts of visible region. The use of costly and synthetic dyes having relatively better electrical performance (but that may be only marginal better, so insignificant) will not serve our purpose because cost of such dye may be drastically higher, but results will be comparable to cheap and renewable sensitizer. The natural photosensitizer offers even more advantages like greater photo stability and regeneration as in photosynthesis due to extensive pie framework and tetra pyrrole nucleus structure whereas synthetic dyes are photo decayed and have no regeneration power as their pie framework is not so extended. Therefore, the use of natural photosensitizers in

photogalvanic cells provides tremendous opportunity for the development of alternative sustainable technology of solar power and storage.

The practical and final aim of all the solar techniques including photogalvanic cells is to meet the energy needs of society. For this, our main focus should be on renewable methods with actual electrical output and cost of the cell. Therefore, I am of the view that performance of the photogalvanic cells is nearly same for various single and mixed dyes (synthetic) and as well for crude extract for practical purpose. Therefore, we should focus on cheap and eco-friendly sensitizers like crude extract to take benefit of cost and clean environment.

The researchers in the field of photogalvanic cells are trying this and that dye sensitizer. But, the performance of various sensitizers is nearly same as observed in the present study. Therefore, I suggest the use of sensitizers like spinach extract (instead of synthetic dye photosensitizers) and designing of new electrodes for further enhancement in electrical output of photogalvanic cells.

It is fact that the results presented by me are quite similar, no matter it is any single dye or any mixed dyes. But, it is to be noted that I have not said that results are identical for all single and mixed dyes. The electrical values are not identical, but nearly of the same order for all single/mixed dyes, as well for crude spinach extract.

My view that electrical performance of various single and mixed sensitizers is nearly same (not significantly different, whereas their economic and environmental cost may be drastically different) is supported by various studies on dye sensitized solar cells. Chen et

al. has reported nearly same Voc ( $\sim 0.4$  volt) and current for various dyes (current is only marginally different)<sup>32</sup>.

Griffith et al. has reported that solar to-electrical power conversion efficiency of each mixture surpassed those of either dye individually, increasing from 0.4% for FbC and 0.7% for ZnNC to 2.1% for the best mixture. The mixture efficiency exceeds the sum of the two individual dyes, exhibiting an increase of 300 % efficiency<sup>33</sup>. But, I see that for practical purpose of daily life, the efficiency shown by FbC, ZnNC, and mixed FbC + ZnNC sensitizers is nearly same. To say an increase of 300 % efficiency is statistically incorrect as correct presentation has been real magnitude not percentage.

Santos et al. has also reported nearly same photovoltaic parameters for various sensitizers measured under Air Mass 1.5 calibrated white light with  $100 \text{ mWcm}^{-2}$  intensity. The Voc (V) for FbNC, FbC, ZnNC, and ZnC is 0.438, 0.576, 0.500, and 0.594, respectively. The FF for FbNC, FbC, ZnNC, and ZnC is 0.41, 0.62, 0.56, and 0.63, respectively. The CE for FbNC, FbC, ZnNC, and ZnC is 0.02, 0.44, 0.17, and 1.62, respectively (CE difference insignificant for practical purpose). The dye excited state oxidation potential, dye ground state oxidation potential, and band gap energy of the dyes is also of the same order for all FbNC, FbC, ZnNC, and ZnC<sup>34</sup>.

Noor et al. have reported FF 0.35, 0.34, 0.41, 0.36 ; Voc (V) 0.76, 0.36, 0.36, 0.36; CE (%) 2.17, 0.37, 0.24, 0.42 respectively for N3, Anthocyanin, Chlorophyll, mixed Anthocyanin + Chlorophyll sensitizers in this sequence<sup>35</sup>. For practical purpose of daily life, the parameters are nearly same.

In the present research work, the results so obtained are higher and very encouraging vis-à-vis reported results for photogalvanic<sup>26, 36-40</sup> as well as photovoltaic techniques<sup>41</sup>.

I don't attribute higher results in present study to the usage of spinach extract as all other single dye or mixed dyes have nearly same result. I attribute higher result to the use of surfactant sodium lauryl sulphate (NaLS) and small Pt ( $0.8 \times 0.2 \text{ cm}^2$ ). The Surfactants like NaLS improves the cell performance (i) by suppressing the thermal back electron transfer, (ii) by enhancing the processes of electron transfer to photosensitizer, and in turn to Pt electrode, and (iii) by enhancing the solubility<sup>42</sup> and stability<sup>43</sup> of the sensitizer molecules.

The thermal back electron transfer process reduces the cell efficiency, and surfactants improve the cell efficiency by suppressing this back electron transfer process<sup>42</sup>.

The reductant donates electron to the sensitizer, and these excess electrons on the sensitizer molecules are transferred to Pt electrode<sup>42</sup>. The photoinduced electron transfer from surfactant to the dye photosensitizer through a charge transfer (CT) interaction enhances the processes of electron transfer to photosensitizer<sup>44</sup>, and in turn to Pt leading to higher current and cell performance.

The more solubility of dye inhibits dye aggregation leading to availability of more dye molecules for photogalvanics<sup>45</sup>.

Long sensitization time results in decreased solar cell efficiency because of decreased efficiency of electron injection<sup>31</sup>. The charging time in previous works is very long. The charging time for each cell in this manuscript is short. This short time may be the reason for higher efficiency in present work.

In present work, the electrical parameters for spinach extract based photogalvanic cell using singly distilled water are  $V_{oc}$  938 mV (0.938 V),  $i_{sc}$  1050  $\mu\text{A}$  ( $J_{SC} = 13 \text{ mA cm}^{-2}$ ),



$P_{pp}$  264  $\mu$ W, CE 8.49 %, and  $t_{0.5}$  50 min. For other photosensitizers, the results are also of the same order.

This  $J_{sc}$  of of the order of 13  $mWcm^{-2}$  is well within the limits laid down by Lambert–Beer law and Shockley–Queisser limit (maximum solar conversion efficiency around 33.7 % assuming a single p-n junction with a band gap of 1.34 eV using an AM 1.5 solar spectrum). It is also to be noted that in some cases result may be higher than the limits laid down by Lambert–Beer law and Shockley–Queisser limit. For example, at 1 sun illumination,  $J_{sc}$  180  $mA cm^{-2}$  is reported, which is higher than that predicted from the Lambert–Beer law and Shockley–Queisser limit<sup>46</sup>.

### 3. Conclusion

The comparative photogalvanics of various single photosensitizers, various mixed photosensitizers, and natural photosensitizer(s) present in crude spinach extract has been studied in this work. This study shows that the mixed photosensitizers shows more or less same electrical performance as that for single photosensitizers under observed conditions. Thus, under similar conditions, the use of mixed dyes (synthetic) offers no extra advantage over use of single dye, and over crude spinach extract. Therefore, it is better to use crude spinach extract for solar power and storage through photogalvanic cells as this use will provide for fabrication of cheap and relatively more eco-friendly photogalvanic cell devices. Therefore, I suggest that we should focus on cheap and eco-friendly natural photosensitizers like chlorophylls present in spinach extract as for practical purpose of application in daily life as the photogalvanics is not significantly dependent on nature of sensitizers.

## Methods Summary

### 1. Chemicals

The dyes (Sudan-I, Rhodamine B, Fast Green FCF, Brilliant Cresyl Blue, Naphthol Green B) as photosensitizer, aqueous crude Spinach Extract as source of natural photosensitizers (see **sec.1.1 of SI**), M/100 Fructose as reductant, M/10 Sodium lauryl sulfate (NaLS) as surfactant, and 1M NaOH as alkaline medium have been used. M/500 solution of each dye has been used. All the solutions except Sudan-I have been prepared in single distilled water, and kept in amber colored containers to protect them from sunlight. Solution of Sudan-I (insoluble in water) has been prepared in ethyl alcohol.

The natural photosensitizers present in spinach extract were not separated for use, but the crude extract as such was used. We have avoided separation of natural photosensitizers for reasons, (i) our aim is the solar energy conversion and storage through development of a technique-which is simple, eco-friendly, close to nature and cheap- in simplest way. The separation step will avoidably complicate our technique. Therefore, we have used resources in the form in which they are available in the nature, (ii) we view that use of separated natural photosensitizers (e.g., Chlorophyll a & b, etc.) will not offer any additional advantages, and (iii) the separation of chlorophyll will be self-defeating as we do not use photo-sensitizer alone, but photo-sensitizer with reductant, NaOH and surfactant.

### 2. Experimental and calculation method

The experimental set up consists of a H-cell, digital pH meter, microammeter, a carbon pot log 470 K device (for changing the resistance of circuit), and a circuit key, which are

connected together as shown in photogalvanic cell set-up (Fig.S7). The artificial light emitted from 200 wattage incandescent bulb has been used to charge the cells.

Initially, the circuit is kept open and cell is placed in dark until it attains a stable potential (dark potential- $V_{\text{dark}}$ ). Then, the Pt electrode is exposed to diffused sun radiations. On illumination; the photopotential (V) and photocurrent (i) are generated by the system.

After charging of the cell, the cell parameters like maximum potential ( $V_{\text{max}}$ ), open-circuit potential ( $V_{\text{oc}}$ ), maximum current ( $i_{\text{max}}$ ) and equilibrium current ( $i_{\text{eq}}$ ) or short-circuit current ( $i_{\text{sc}}$ ) are measured. The study of i-V characteristics of the cell [done by observing potential at different direct currents by varying resistance (calculated by Ohm law) of the circuit] shows the highest power at which cell can be used.

The cell is operated at highest power (i.e., power at power point -  $p_{\text{pp}}$ ) at corresponding external load, current (i.e., current at power point -  $i_{\text{pp}}$ ) and potential (i.e., potential at power point- $V_{\text{pp}}$ ) in order to study its performance by observing change in current and potential with time.

The cell performance is studied in terms of half change time ( $t_{0.5}$ ), conversion efficiency (CE) and fill factor (FF) in dark. The time taken for fall in the power of the cell to its half value of power at power point is called  $t_{0.5}$  (which is measure of storage capacity of the cell). The average rate of change of current over  $t_{0.5}$  period ( $\Delta i/\Delta t$ ) is calculated from  $(i_{\text{pp}} - i_{t_{0.5}})/t_{0.5}$ , where  $i_{t_{0.5}}$  is current at  $t_{0.5}$ . The potential corresponding to  $i_{t_{0.5}}$  is  $V_{t_{0.5}}$ . The charging time (t) is calculated as, charging time = (time at which  $V_{\text{max}}$  is obtained) – (time at which illumination is started). The photopotential ( $\Delta V$ ) is equal to  $V_{\text{max}} - V_{\text{dark}}$ .

The initial pH of the reaction mixture has been calculated by formula,  $\text{pH} = 14 - \text{pOH}$ .

The CE and FF of the cell are calculated from equations (1) and (2), respectively.

$$FF = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \dots\dots (1) ; CE = \frac{V_{pp} \times i_{pp} \times FF}{PA} \times 100\% \dots\dots (2)$$

Where  $P$  and  $A$  is artificial illumination intensity ( $10.4 \text{ mWcm}^{-2}$ ) and Pt electrode area ( $0.08 \text{ Cm}^2$ ), respectively.  $V_{pp} \times i_{pp}$  is expressed in  $\text{mW}$ .

The size of open window (illuminated area of the cell) of illuminated arm has not been used for calculating the efficiency as natural sunlight is available naturally and free of cost. So to illuminate small or large area of cell does not affect the cost and environment. But, the use of small or large Pt electrode affects the cost and environment. Therefore, Pt electrode area has been taken as standard for calculating the efficiency as cost and environment is affected by Pt area. Use of small Pt electrode area will be less costly and more eco-friendly as low demand for Pt will require less production of Pt leading to reduction in pollution. Therefore, I am of the view that Pt electrode area is the better choice for calculation of efficiency.

## References

1. L. Zhao, J. Yu, J. Fan, P. Zhai and S. Wang, *Electrochem. Commun.* 2009,**11**, 2052.
2. R. F. Service, *Science*, 2011, **332** (6027), 293.
3. E.K. Rideal and E.G. Williams, *J. chem. Soc. Trans.*, 1925,**127**, 258.
4. E. Rabinowitch, *J. Chem. Phys.*, 1940, **8**, 551.
5. A. E. Potter Jr. and L.H. Thaller, *Sol. Energy*, 1959, **3**, 1.
6. W. J. Albery and M. D. Archer, *Nature*, 1977, **270**, 399.
7. R. Gomer, *Electrochim. Acta.*, 1975, **20**,13.
8. F. K. Fong, J. S. Polles, L. Galloway and D. R. Fruge, *J. Am. Chem. Soc.*, 1977,**99**, 5802.

9. A. Zeichner, J. R. Goldstein and G. Stein, *J. Phys. Chem.*, 1978, **82**, 1687.
10. C. Daul, O. Haas, A. Lottaz, A.V. Zelewsky and H.R. Zumbrennen, *J. Electroanal. Chem.*, 1980, **112**, 51.
11. H. Shiroishi, K. Yuuki, S. Michiko, H. Takayuki, N. Tomoyo, T. Sumio and K. Masao, *J. Chem. Soft.*, 2002, **8**, 47.
12. S. Pokhrel and K.S. Nagaraja, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 244.
13. N. S. Dixit and R. A. Mackay, *J. Phys. Chem.*, 1982, **86**, 4593.
14. K. M. Gangotri and S. Pramila, *Energy Sources Part A.*, 2006, **28**, 149.
15. A.S.N. Murthy and K.S. Reddy, *Sol. Energy*, 1983, **30**, 39.
16. S.C. Ameta, S. Khamesra, A. K. Chittora and K.M. Gangotri, *Int. J. Energy Res.*, 1989, **13**, 643.
17. K. M. Gangotri and C. Lal, *Energy Sources Part A.*, 2001, **23**, 267.
18. K.M. Gangotri and V. Indora, *Sol. Energy*, 2010, **84**, 271.
19. S. Madhwani, R. Ameta, J. Vardia, P. B. Punjabi and V. K. Sharma, *Energy Sources Part A.*, 2007, **29**, 721.
20. Pooran Koli, *Applied Energy*, 2007, **118**, 231.
21. S. Pramila and K.M. Gangotri, *Energy Sources Part A.*, 2007, **29**, 1253.
22. K. R. Genwa and Mahaveer, *Indian J. Chem., Sect A.*, 2007, **46 A**, 91.
23. C. Lal, *J. Power Sources*, 2007, **164**, 926.
24. K. R. Genwa and A. Chouhan, *J. Chem. Sci.*, 2004, **116**, 339.
25. P. Gangotri and K. M. Gangotri, *Energy Fuels*, 2009, **23**, 2767.

26. M.K. Bhimwal and K.M. Gangotri, *Energy*, 2011, **36**, 1324.
27. U.Sharma, P.Koli and K.M. Gangotri, *Fuel*, 2011, **90**, 3336.
28. K. M. Gangotri, C. Lal, Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy, 2005, **219**(5), 315.
29. K.K.Rohatgi Mukherjee, *Fundamentals of Photochemistry*, New Age International Publishers, India, 2nd edn., 1986, ch.3, pp.77-81.
30. J. Stur, M. Bos and W. E. V.Linden, *Anal. Chim. Acta*, 1984, **158**, 125.
31. H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S. E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chábera, A. P. Yartsev, and V. Sundström, *J. Phys. Chem. A*, 2011, **115**, 3679.
32. Z. Chen, F. Li and C. Huang, *Curr. Org. Chem.*, 2007, **11**, 1241.
33. M.J.Griffith, A. J. Mozer, G.Tsekouras, Y.Dong, P.Wagner, K.Wagner, G.G.Wallace, S. Mori, and D. L. Officer, *Appl. Phys. Lett.*, 2011, **98**, 163502.
34. T. D. Santos, A. Morandeira, S. Koops, A. J. Mozer, G. Tsekouras, Y. Dong, P. Wagner, G. G. Wallace, J. C. Earles, K. C. Gordon, D. L. Officer and J. R. Durrant, *J. Phys. Chem. C*, 2010, **114**, 3276.
35. M. M. Noor, M. H. Buraidah, S. N. F. Yusuf, M. A. Careem, S. R. Majid and A. K. Arof, *Int. J. Photoenergy*, Vol. 2011, DOI:10.1155/2011/960487.
36. K. M. Gangotri, P. Aseri and M. K. Bhimwal, *Energy Sources, Part A.*, 2013, **35**, 312.
37. S. Yadav and C. Lal, *Energy Convers. Manage.*, 2013, **66**, 271.

38. K.R. Genwa and C.P. Sagar, *Energy Convers. Manage.*, 2013, **66**,121.
39. A. Chouhan and K. R. Genwa, *Energy Sources, Part A.*, 2013, **35**,685.
40. P. Koli, U. Sharma and K.M. Gangotri, *Renewable Energy*, 2012, **37**,250.
41. S.H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.
42. E. J. J. Groenen, M. S. De Groot, R. De Ruiter, N. De Wit, *J. Phys. Chem.*, 1984, **88**, 1449.
43. M. Havelcova, P.Kubat, I. Nemcova, *Dyes Pigm.*, 1999, **44**, 49.
44. M. Mukhopadhyay, B. B. Bhowmik, *J. Photochem. Photobiol., A*, 1993, **69**, 363.
45. P. P. Solanki and K M Gangotri, World renewable energy congress, Sweden, 2011.
46. P. Krogstrup, H. I.Jorgensen, M. Heiss, O. Demichel, J. V. Holm, M. Aagesen, J. Nygard and A.F. Morral, *Nat. Photonics*, 2013, **7**,306.

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**Table 1. The chemical Compositions of cells fabricated for study of Photogalvanic effect of mixture of photosensitizers**

Cell No.	Volume of M/500 Photosensitizer(s) used to prepare total 25.0 ml mixture	Resultant Concentrations of Photosensitizer(s)
1.	0.38 ml NGB	$3.04 \times 10^{-5}$ M
2.	0.38 ml FCF	$3.04 \times 10^{-5}$ M
3.	0.38 ml BCB	$3.04 \times 10^{-5}$ M
4.	0.38 ml SPE	Conc. not determined & calculated as crude spinach extract was taken
5.	0.38 ml RHD	$3.04 \times 10^{-5}$ M
6.	0.38 ml SUD	$3.04 \times 10^{-5}$ M
7.	0.38 ml of each NGB, FCF; Total 0.76 ml	$3.04 \times 10^{-5}$ M each; Total $6.08 \times 10^{-5}$ M
8.	0.38 ml of each NGB, FCF, SPE; Total 1.14 ml	$3.04 \times 10^{-5}$ M each of NGB & FCF; Total $6.08 \times 10^{-5}$ M + 0.38 ml SPE
9.	0.38 ml of each NGB, FCF, RHD; Total 1.14 ml	$3.04 \times 10^{-5}$ M each; Total $9.12 \times 10^{-5}$ M
10.	0.38 ml of each NGB, FCF, BCB, SPE, RHD, SUD; Total 2.28 ml	$3.04 \times 10^{-5}$ M each of NGB, FCF, BCB, RHD, SUD; Total $15.2 \times 10^{-5}$ M + 0.38 ml SPE
11.	0.38 ml NGB,	$3.04 \times 10^{-5}$ M each
12.	0.13 ml of each NGB, FCF, BCB; Total 0.39 ml	$1.04 \times 10^{-5}$ M each; Total $3.12 \times 10^{-5}$ M
13.	0.09 ml of each NGB, FCF, BCB, SPE; Total 0.36 ml	$0.72 \times 10^{-5}$ M each of NGB, FCF, BCB; Total $2.16 \times 10^{-5}$ M + 0.38 ml SPE
14.	0.07 ml of each NGB, FCF, BCB, SPE, RHD; Total 0.35 ml	0.56 Each of NGB, FCF, BCB, RHD; Total $2.24 + 0.38$ ml SPE
15.	0.06 ml of each NGB, FCF, BCB, SPE, RHD, SUD; Total 0.36 ml	0.48 of each NGB, FCF, BCB, RHD, SUD; Total $2.4 + 0.38$ ml SPE



**Table 2. Summary of solar energy conversion and storage for various individual and mixed photosensitizers**

Cell No.	Photosensitizer(s) with $\lambda_{\max}$ (nm)	Cell performance							
		$V_{oc}$ (mV)	$i_{\max}$ ( $\mu$ A)	$i_{sc}$ ( $\mu$ A)	$P_{pp}$ ( $\mu$ W)	$i_{pp}$ ( $\mu$ A)	CE (%)	FF	$t_{0.5}$ (min.)
1.	NGB (714)	925	1100	900	204.1	420	6.0	0.245	140
2.	FCF (622)	960	1250	1000	186	420	4.36	0.193	27
3.	BCB (622)	1040	1070	850	216.9	450	6.37	0.245	63
4.	SPE (435 & 680)	938	1300	1050	264	600	8.49	0.268	50
5.	RHD (543)	1007	1350	1130	272.4	600	7.81	0.239	26
6.	SUD (476)	1014	1550	1150	316.8	600	10.29	0.271	30
7.	NGB (714), FCF (622)	1000	1350	1100	261	620	7.65	0.237	17
8.	NGB (714), FCF (622), SPE (435 & 680)	973	1200	1025	248.5	520	7.42	0.249	125
9.	NGB (714), FCF (622), RHD (543)	970	1300	1070	249.6	600	7.32	0.240	30
10.	NGB (714), FCF (622), BCB(622),SPE(435&68), RHD(543),SUD(476)	1040	1750	1450	303.6	660	8.84	0.201	19
11.	NGB (714)	1040	2050	1850	401.1	1050	10.54	0.208	260
12.	NGB (714), FCF (622), BCB (622)	1052	2250	1900	434.3	850	11.32	0.217	51
13.	NGB (714),FCF (622), BCB(622),SPE(435&68)	999	2300	1950	464	1000	13.25	0.238	32
14.	NGB(714),FCF(622), BCB(622),SPE(435&68), RHD (543)	1060	2300	1800	405.4	850	10.32	0.212	14
15.	NGB(714),FCF(622), BCB(622),SPE(435&68), RHD(543),SUD(476)	1004	2000	1600	347.2	750	9.00	0.216	31

**Figure legends**

Fig.1 (a, b). Variation of potential with time.

Fig.2 (a, b). Variation of power with current.

Fig.3.Study of cell performance) - Power vs Time,

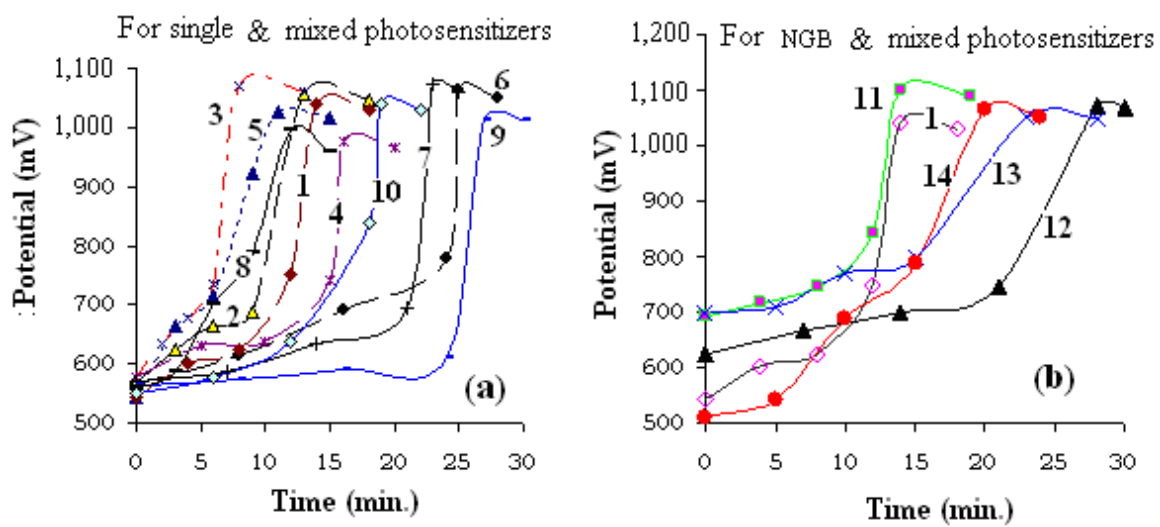
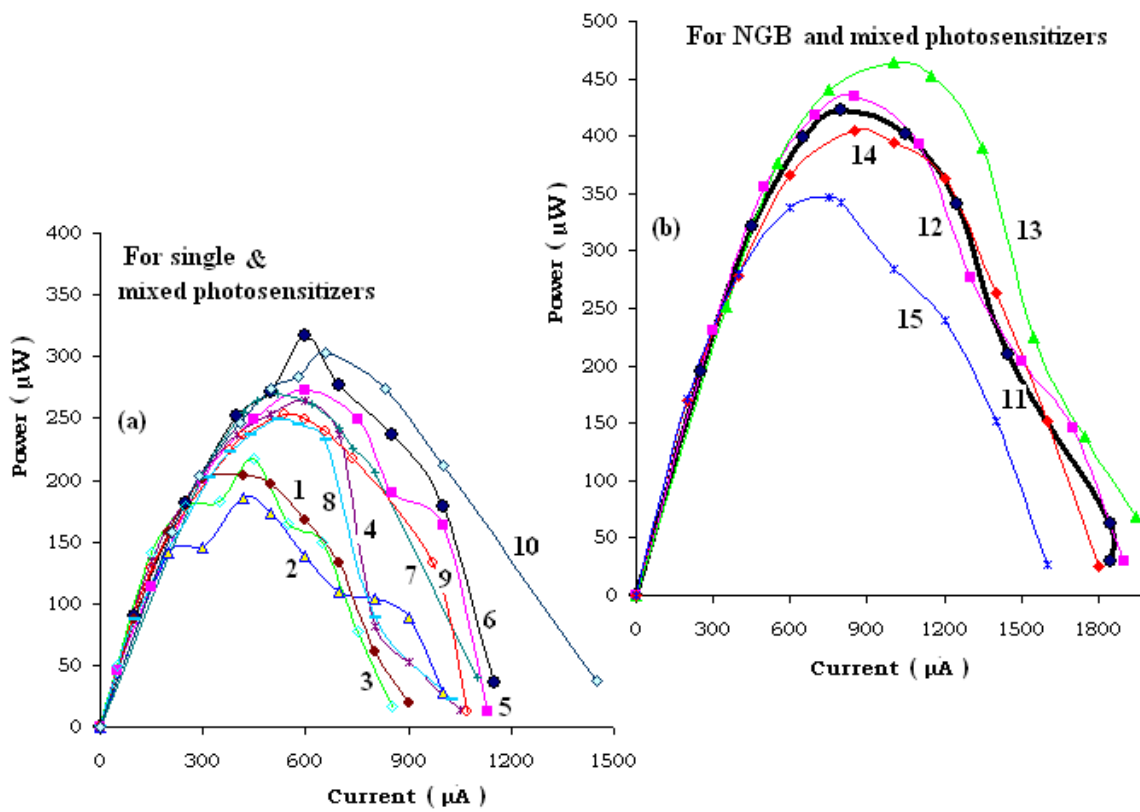


Fig.1



*Fig. 2*



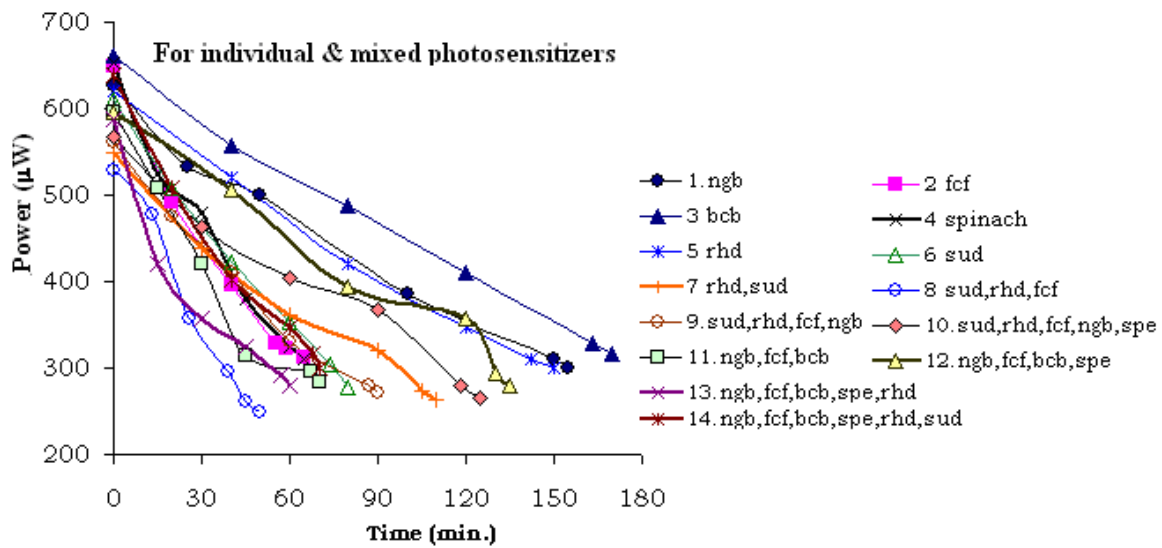


Fig.3.