Use of Pigments Present in the Crude Aqueous Extract of the Spinach for the Simultaneous Solar Power and Storage at Natural Sun Intensity

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The photogalvanic (PG) solar cell technique discussed in the present study has potential for both solar energy conversion and solar power storage at a time. The harvesting of the solar energy using costly, polluting, and synthetic dye sensitizers cannot be a sustainable method. Furthermore, the sensitizers including the natural sensitizers must be capable of showing simultaneous solar energy and conversion at natural sunlight intensity. With this aim, therefore, the PG cell using cheap and easily obtainable aqueous crude spinach extract for harvesting natural sunlight for solar power generation and storage is fabricated and studied. Herein, it is shown that this extract can also be an efficient sensitizer in the PG cell technique for harvesting energy from the natural sunlight by following the same cell fabrication principles as applicable for the synthetic dye photosensitizers at artificial and low illumination intensity. A very good open-circuit potential (1.088 V), steady-state current (50 mA cm⁻²), power output (13.05 mW cm⁻²), and efficiency obtainable (≈13%) at a peculiar external load resistance (322.2 Ω) are observed during the natural sunlight illumination.

1. Introduction

There are semiconductor-based dye-sensitized solar cells (DSSCs),¹⁻³ which directly yields the solar electricity from the sunlight. Similar to DSSCs, the photogalvanic (PG) cell is also a promising technique for getting solar electricity directly from the sunlight with inherent power storage capacity as well. DSSC shows workability even at low illuminating intensity with the fact that angle of light incident on DSSCs does not significantly affect these cells.⁴ Similarly, the PG cells also show workability at low illumination intensity irrespective of the angle of incidence.

The unique property of PG cells lies in their capacity to be charged at low intensity (inside room) as well as to work as a power storage device. The PG cell technique consists of two dissimilar electrodes dipped in the very dilute electrolyte solution containing artificial/natural photosensitizer(s), reductant(s), alkali (NaOH), and surfactant(s). Photovoltaic (PG) conversion by a macro-molecular thionine organic dye film photosensitizer-ferrous salt inorganic reductant chemical system,⁵ a tolulafranine organic dye photosensitizer-ethylenediaminetetraacetic acid (EDTA) organic reductant system,⁶ and a thionine dye photosensitizer solution-ferrous salt inorganic reductant chemical system⁷ has been reported.

The PG cell based on various inorganic compounds,⁸⁻¹⁰ organic dye photosensitizers with organic reductants,¹¹⁻¹⁴ and surface-active reagents dissolved in the water (prepared from deionization followed by distillation in the presence of KMnO₄) has been widely studied. A new photosensitizer (methyl yellow)—reductant (formic acid) couple in the PG cells—has also been recently reported.¹⁵ The synthetic organic dye (metanil yellow)-based PG cell has shown impressive solar energy conversion (649.6 μW, 2250 μA, and 8.12%) and solar power storage (as 59 min as half-time).¹⁶ In comparison with the inorganic colorants, the organic dyes have higher absorbance, low cost, and more diversity in the molecular structure. The higher absorbance enables organic dyes to absorb more sunlight, and therefore, the less amount of dye in the form of a very dilute solution suffices for the fabrication of the PG cells. But, the synthesis of organic dyes and their disposal is associated with an environmental cost. The efficiency of PG cells heavily depends on the dye stability, nature of electrodes, and rate of electrons transfer kinetics. The lifetime of photoexcited species such as sensitizers is very short, so these short-lived species have to reach working electrode within their lifetime through fast kinetics. To overcome this problem, Mahmoudzadeh and Maddern¹⁷ have reported a study on the vertical illumination through the electrodes of the cell to ensure spreading of the absorption of the sunlight and, hence, generation of the electrons through the depth of the cell device. The use of relatively more stable excited species of natural sensitizers (such as chlorophyll “a”) as a result of very extensive pie framework may also be a solution to meet the requirement of fast kinetics. In the long term, the use of...
synthetic organic dyes in the fabrication of PG cells cannot be a sustainable option. It is because the photosensitive materials form one of the main constituents of the PG solar cell technique and also a prime component for leading to the improvement in cell performance. Almost all the studies reported by researchers on PG cells have focused on synthetic dye sensitizers that too in artificial and low illumination intensity. This is the research gap, which needs to be bridged by exploring the possibilities of use of natural resources such as spinach extract in PG cells that too in the natural sunlight. Therefore, the use of some naturally occurring light-absorbing materials along has to be an integral part of these cells. The crude aqueous extract of the naturally occurring spinach resource-sensitized PG cell has been studied at the artificial and low illumination intensity with impressive results (384.0 μW, 1750 μA, and 9.22%).[19] But, the reported spinach extract-based cells have the drawback that its workability is shown at very low and artificial illumination intensity only,[19] whereas these cells have to be workable at natural sunlight intensity for day-to-day life applications. Natural sunlight-irradiated Rhodamine B dye-sensitized and surface-active reagent augmented PG solar energy conversion (620.1 μW, 2400 μA, and 7.75%) and storage have been reported recently,[20] but the study on naturally illuminated natural sensitizer spinach extract-based PG cells has not attracted attention of the researchers yet. The feasibility of working of PG cells in a steady and stable manner at characteristics external load is also not reported so far. Comparable efficacy of the spinach extracts sensitizer (with additional advantages of photostability and the presence of cosensitizers) as that of the synthetic dye sensitizers is already established experimentally for PGs.[21] A cosensitization process enhances the efficiency of DSSCs.[22] Efficacy of natural pigment photosensitizers has also been proved in DSSCs.[23–28]

The role of surfactants in augmenting the solvability and photosolidity of the photosensitizer’s molecules leading to hike in the solar energy conversion efficiency (CE) of the DSSCs is also experimentally established.[29,30] Surfactants, such as cetetyltrimethylammonium bromide (CTAB),[29] Tween 80,[30] and sodium laureyl sulfate (NaLS),[29,30] have been studied to enhance the performance of PG cells by the way of decreasing aggregation of dye molecules. Role of surfactants as the CTAB,[31] cetetylpyridinium chloride (CPC),[31] lithium dodecylsulfate (LiDS),[31] and Triton X-100[31] has been studied on aggregation of chlorophyll “a” (a natural photosensitizer used in the present manuscript). Surfactants have been observed to show shift in absorption bands of chlorophyll “a” photosensitizer.[31]

With this background of gap, limitations, and challenges in the research area of the PG cells, the use of a crude extract of the leaves of the spinach (a naturally occurring resource) along with the surfactant was undertaken at natural sunlight illumination in the present study. The purpose of the present work was to see 1) whether crude extract of the leaves of the spinach (a naturally occurring resource) can photosensitize PGs at natural sunlight; if yes, then at what efficiency vis-a-vis synthetic dye sensitizers? 2) Whether the principles governing the synthetic organic dye-based PG cells also applicable to the working of PG cells based on crude aqueous extract? 3) Whether the fabrication of crude extract-based PG cell will follow the same working fundamentals as governing the PG cells with artificial sensitizer in artificial and low illumination intensity? and 4) to see whether the PG cell is able to perform in a stable and steady manner at maximum power at characteristic external load during the illumination with natural sunlight. With this aim, the study of the PGs of the crude aqueous extract of the leaves of spinach with D(-) fructose (reductant), NaLS as the surface-active reagents, saturated calomel electrode (SCE; terminal of combination electrode), and platinum (Pt) electrode of a very small dimension was undertaken with natural sunlight illumination.

2. Experimental Section

2.1. Chemicals and Apparatus

Aqueous crude spinach extract[32–37] as a source of natural photosensitizers, M/100 fructose as reductant, M/10 sodium laurel sulfate (NaLS) as surfactant, and 1 m NaOH as alkaline medium have been used. All the solutions have been prepared in single distilled water. Digital pH meter-Systronics Model: 335 and microammeter-OSAW has been used for measuring the potential in millivolt–mV and the current in microampere–μA. Digital pH meter was purchased from the Systronics India Ltd. Company, Ahmedabad, Gujarat (India). Microammeter was purchased from the Osaw Industrial Products Pvt. Ltd., Ambala, Haryana (India).

Sodium laurel sulfate was purchased from the Ases Chemical Works, Jodhpur, Rajasthan (India). It is a white powder soluble in water. Its characteristics are IUPAC name Sodium dodecyl sulfate (SDS), M.F. C12H25SO4Na, M.W. 288.3 g mol⁻¹. Purity (Active Matter) 94% minimum (impurity of chloride, sulfate, moisture, unreacted oil, etc.), pH (of 10% solution) 7.5–9.5 at 25 °C, density 1.01 g cm⁻³, melting point 206 °C, and Chemical Abstracts Service (CAS) number 151-21-3. The fructose (99.8% assay) and sodium hydroxide (98% assay) were also purchased from the Ases Chemical Works, Jodhpur, Rajasthan (India).

Spinach has some peculiar characteristics, which prompted us to use it as a source of the natural sensitizer. Spinach is an easily available annual plant. It is a safe and edible plant. Fresh spinach is a convenient source of chlorophyll “a” and “b.” Chlorophyll absorbs radiation almost over the range particularly in the blue-violet (470 nm) and red (650–700 nm). Aqueous spinach extract was obtained from the fresh spinach leaves (botanical name Spinacia oleracea) Aqueous spinach extract was obtained, as 1) fresh spinach leaves (botanical name Spinacia oleracea) were washed with water; 2) the washed and wet leaves (50 gm) were crushed in the presence of a little water (10 mL) in a jar of electric mixer; 3) then, crushed matter was filtered with an ordinary filter paper; 4) filtrate was left undisturbed for sometime to allow sedimentation of fibrous and other matter; and 5) the transparent liquid above sediment was used as aqueous spinach extract for photosensitization of solution in PG cell.

2.2. Experimental and Calculation Method

The experimental setup consists of an H-cell (PG cell), natural sunlight, digital pH meter-Systronics Model: 335 (which measures potential in millivolt–mV), microammeter-OSAW (which measures current in microampere–μA), a carbon pot log 470 K device (for changing the resistance of circuit), and a circuit
key, which are connected together, as shown in PG cell setup (Figure 1). Natural sunlight has been used to charge the cell.

Initially, the circuit is kept open, and the cell is placed in dark till 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 such as 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 the \(V-i\) characteristics of the cell by observing potential at different direct currents by varying the resistance (calculated by Ohm law) of the circuit shows the highest power at which the cell can be used. The cell is operated at the highest power (i.e., power at power point—\(P_{\text{pp}}\)) at the corresponding external load, current (i.e., current at power point—\(i_{\text{pp}}\)), and potential (i.e., potential at power point—\(V_{\text{pp}}\)) for study of its performance by observing change in current and potential with time.

The cell performance is studied in terms of half-change time (\(t_{0.5}\)), 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 the 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 \((i_{\text{pp}} - i_{0.5})/i_{0.5}\), where \(i_{0.5}\) is current at \(t_{0.5}\). The potential corresponding to \(i_{0.5}\) is \(V_{0.5}\). The charging time (\(t\)) is calculated as, charging time = (time at which \(V_{\text{max}}\) is obtained) – (time at which illumination is started). Photopotential (\(\Delta V\)) is equal to \((V_{\text{max}} - V_{\text{dark}})\). The CE and FF of the cell are calculated as \([V_{\text{pp}} \times i_{\text{pp}} \times 100\%]/[P_{\text{A}}]\) and \([V_{\text{pp}} \times i_{\text{pp}}]/[V_{\text{oc}} \times i_{\text{sc}}]\), respectively. Here, the “P” and “A” are the average natural sunlight intensity (\(\approx 100\, \text{mW cm}^{-2}\)) and Pt electrode area (0.08 cm²), respectively. \(V_{\text{pp}} \times i_{\text{pp}}\) is expressed in mW.

Performance values (power and current) have been normalized to the area dimension of Pt electrode. 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, illuminating 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, the Pt electrode area has been taken as standard for normalization, as cost and environment are affected by Pt area. The use of small Pt electrode area will be less costly and more eco-friendly, as low demand for Pt will need less production of Pt, leading to the reduction in pollution. The initial pH of the reaction mixture has been calculated by the formula, pH = 14-pOH.

The sunlight incident angle was \(88^\circ–84.75^\circ\), and the light intensity was \(97.18\, \text{mW cm}^{-2}\). The cell was charged for 13 min from local time 12:48 AN-1:01 AN (i.e., incident angle of \(88^\circ–84.75^\circ\)).

The experiments were done at Jodhpur (India) having geographical parameters as hour angle 12.08°; local solar time 12:48 AN, declination (-)13.12°, latitude 26.2°, longitude 73.02°, azimuth 198.09°, zenith 41.04°, elevation 48.96°, and time zone 5.5. The experiments have been done in natural environment (outside the laboratory) conditions in day time during natural sunlight (temperature \(\approx 31^\circ\text{C}\), humidity \(\approx 21\%\), wind \(\approx 6\, \text{km h}^{-1}\), and atmospheric pressure \(\approx 1.011\, \text{bar}\)). The experiments were done in uncontrolled conditions; therefore, the environmental conditions are only of approximate value. All electrical parameters (such as current, potential, power, efficiency, etc.) of the cell have been measured under these environmental conditions.

The already published work is related to the Rhodamine B sensitizer-fructose reductant at artificial and low sun intensity (from incandescent tungsten bulb of the 200 wattage, light intensity 10.4 mW cm⁻²) in controlled laboratory conditions[16] Work in the present research is different and is related to the crude aqueous extract of the leaves of spinach as sensitizer-fructose (reductant) at natural sunlight illumination (\(\approx\) average light intensity 100 mW cm⁻²) in natural conditions of daily life (out of laboratory in uncontrolled conditions).

![Figure 1](image.png)

**Figure 1.** Schematic of the experimental setup of PG cells (A—micrometer, K—key, R—resistance, and V—digital pH meter).

3. Results and Discussion

The PG cell having a total 68 mL electrolyte solution consisting of the 3.8 mL of crude aqueous extract of the spinach, 10 mL of NaLS (M/10), 16 mL of fructose (M/100), 36 mL of NaOH (1 M) and 2.2 mL of water solvent was studied. The unionized water solvent was prepared with the help of an ion exchanger method, and this water solvent has been used to dilute the electrolyte solution up to 68 mL to keep the solution resistance and resultant concentrations similar in each cell. The resultant concentrations of the electrolyte solution and cell fabrication parameters are \(2.35 \times 10^{-3}\) M fructose reductant concentration, 1.47 \(\times 10^{-2}\) M NaLS surfactant concentration, 13.72 pH, 6.3 cm diffusion length (\(D_t\)). Pt as anodic terminal (dimensions 4 mm length \(\times\) 2 mm width), and calomel electrode (saturated) terminal of combination electrode as cathodic electrode. This PG cell consisting of these parameters was put in the sunlight (\(\approx 100\, \text{mW cm}^{-2}\) intensity) for charging.

At cell fabrication parameters including chemical compositions as mentioned in the first para of this subsection, the electrical output characteristics of the PG cell in the form of potential,
current, power, etc. are as 0.547 V (dark potential, \(V_{\text{dark}}\); 13 min (charging time, \(t\)); 1.095 V (maximum or highest potential, \(V_{\text{max}}\); 1.088 V (open-circuit or equilibrium potential, \(V_{\infty}\); 68.75 mA cm\(^{-2}\) (maximum current, \(i_{\text{max}}\); 50 mA cm\(^{-2}\) (short-circuit current, \(i_{\text{sc}}\); 13.05 mW cm\(^{-2}\) (power at power point, \(P_{\text{pp}}\); 77 min (storage capacity, \(i_{\text{oc}}\); \(\approx 13\%\) (efficiency of the solar energy conversion, CE); and 0.23 (FF of the solar cell). The FF is not so proportionately high with respect to the CE. The lower FF of the PG cell may be attributed to the photodecay of the dye, higher series resistance type, and the small value of shunt resistance type. The results reported in this article have been tested from the Indian reputed national laboratories/institutes (Department of Chemistry, JNV University, Jodhpur; Government PG College Tonk, MDS University, Ajmer) where similar work on PG cells is being.

### 3.1. Mechanism of Solar Power Generation and Storage

The PG devices reported in this manuscript use crude spinach extract along with NaLS, NaOH (high pH), and fructose. The crude aqueous spinach extract has a pigment complex of chlorophyll “\(a\)”-protein, carotenoids, chlorophyll “\(b\)” and other ancillary pigments. The chlorophyll “\(a\)”-protein complex is the main light-sensitive material, which causes conversion of visible light into the solar power and storage. Other subsidiary molecules such as carotenoids, chlorophyll “\(b\)” and other pigments help main pigment’s (chlorophyll “\(a\)” protein) protection by absorbing excess solar energy, and they are also thought to transfer that energy to main pigment.

On the basis of already published literature,\(^6,29–31,38\) the photoexcited state of pigment chlorophyll “\(a\)” molecule is thought to receive an electron from the reductant fructose molecule. The excited reduced pigment molecule and/or energy quenched reduced pigment molecule shed excess electron to the working electrode Pt. It can be explained, as the absorbed photon energy converts ground state of the pigment sensitizer molecule to excited state of the sensitizer molecule. The fate of excited state is the fluorescence; intersystem crossing, phosphorescence, collision-induced deactivation to the ground state, and photochemical reaction. Through the photochemical reaction between the excited state sensitizer molecule and the reductant molecule, the excited state sensitizer molecule is converted into its energy quenched reduced state having an excess electron. The reduced state of sensitizer molecule having an excess electron cannot accommodate this excess electron for long time. Therefore, the reduced state of sensitizer molecule shed this excess electron to the Pt electrode. This excess electron then moves through the external circuit to the cathodic electrode situated in the nonilluminated chamber of the H-shaped cell. In the nonilluminated chamber, the photosensitizer pigment molecule is thought to accept electron(s) from the cathodic electrode to form its one electron reduced (semiform) or two electron reduced forms (leuco form). The reduced pigment molecule shed extra electron to the oxidized fructose reductant molecule to give original photosensitizer pigment molecules and reductant molecules in dark chamber.\(^29–31\) One electron or two electron reduced sensitizer molecules are the electroactive substances in the light illuminated chamber. The nonilluminated chamber has the ground-state sensitizer molecule as an electroactive species. It means that the ground-state sensitizer molecule has reox potential of the order of that of the reference electrode in the dark chamber. Therefore, it is electrically active or responsive and participates in the electron acceptance from the external circuit through the electrode in the dark chamber. The molecule of fructose reductant acts as an electron transferring agent of giving electron to the photoexcited excited sensitizer molecule and accepting electron from the reduced ground-state sensitizer molecule.\(^31\) In electrolyte, the motion of the ions and other species is governed by the diffusion forces as a result of concentration difference. The increased diffusion forces are estimated to enhance the overall cell performance.\(^6,38\)

### 3.2. Steady-State Performance of the Cell with Time

On illumination of this PG cell with natural sunlight, the potential increases slowly and regularly in the beginning, and later on, it increases abruptly to the highest potential value called maximum potential (\(V_{\text{max}}\)). After sometime of this maximum potential, it decreases by a small value and becomes quite constant value called open-circuit potential (\(V_{\infty}\)). On illumination of this PG cell, the change in photocurrent also follows the same pattern as is applicable to change in photopotential. The photocurrent rises steadily and regularly to a maximum current (\(i_{\text{max}}\)) value, which, after sometime, then decreases to a quite constant value called short-circuit current (\(i_{\text{sc}}\)). This pattern of change of photocurrent shows the presence of a rate-determining step, most likely a recycling process of the one electron reduced state (semi-state) or two electron reduced state (leuco state) of photosensitizer and the oxidized state of the reducing substance in the nonilluminated chamber, which emerges rather late after the initial rapid reaction.\(^31\)

The cell does give highest power at some characteristic value of the current and external load resistance. It has been determined by measuring various potential values at various corresponding current values at various magnitude of the external load resistance. The curve between potential values and its corresponding current shows current–voltage characteristics of the PG solar cell. An external load resistance of 322.2 \(\Omega\) with the corresponding current of 22.5 mA cm\(^{-2}\) enables cell to give a power of 13.05 mW cm\(^{-2}\) (power at power point) (Table 1 and Figure 2).

At characteristic load (322.2 \(\Omega\)) and during the illuminating conditions, the PG cell is also able to generate current and potential in a steady-state manner (Table 2 and Figure 3). During the illumination of the cell, the magnitude of the extracted power from the cell remains nearly the same (Table 2 and Figure 3). The cell was put under observation continuously for 2 h during illumination. It has been observed that the cell was generating a current of 21.75 mW cm\(^{-2}\), a power of 10.89 mW cm\(^{-2}\), and a potential of 0.501 V. For over 2 h, the magnitude of these electrical parameters remained nearly the same. At the end of the 2 h, the magnitude of generated current, power, and potential was 22.68 mW cm\(^{-2}\), 10.53 mW cm\(^{-2}\), and 0.464 V, respectively. Such a stability of crude spinach extract-based PG cell is attributed to the photostability of robust chlorophyll molecule, surfactant-enhanced stability of chlorophyll molecule, extensive optical length of pie framework of chlorophyll molecule, the
Table 1. Variation of potential and power with current (i–V characteristics of cell).

| Current [mA cm\(^{-2}\)] | Potential [V] | Power [mW cm\(^{-2}\)] | Resistance [\(\Omega\)] |
|---------------------------|---------------|---------------------------|-------------------------|
| 50                        | 0.016         | 0.80                      | 4                       |
| 47.5                      | 0.039         | 1.85                      | 10.2                    |
| 45                        | 0.054         | 2.43                      | 15                      |
| 42.5                      | 0.076         | 3.23                      | 22.3                    |
| 40                        | 0.107         | 4.28                      | 33.4                    |
| 37.5                      | 0.166         | 6.22                      | 55.3                    |
| 35                        | 0.227         | 7.94                      | 81                      |
| 32.5                      | 0.293         | 9.52                      | 112.6                   |
| 30                        | 0.362         | 10.86                     | 150.8                   |
| 27.5                      | 0.437         | 12.01                     | 198.6                   |
| 25                        | 0.512         | 12.80                     | 256                     |
| 22.5 (\(J_{pp}\))        | 0.580 (\(V_{pp}\)) | 13.05 (\(P_{pp}\)) | 322.2, CE =13% |
| 20                        | 0.639         | 12.78                     | 399.3, FF = 0.23       |
| 17.5                      | 0.684         | 11.97                     | 488.5                   |
| 15                        | 0.736         | 11.04                     | 613.3                   |
| 12.5                      | 0.770         | 9.62                      | 770                     |
| 10                        | 0.798         | 7.98                      | 997.5                   |
| 7.5                       | 0.812         | 6.09                      | 1333.3                  |
| 5                         | 0.867         | 4.33                      | 2167.5                  |
| 2.5                       | 0.907         | 2.26                      | 4535                    |
| 0                         | 1.080         | 0                         | \(\infty\)             |

\(^{a}\)In natural sunlight for 3.8 mL of crude aqueous spinach extract, 16 mL of M/100 fructose, 10 mL of M/10 NaLS, 36 mL of 1 L NaOH, 2.2 mL of single distilled water (total volume of solution 68 mL), and Pt of 0.08 cm\(^{-2}\); \(^{b}\)Negative value.

Figure 2. Variation of potential and power with current during illumination after charging of the cell: a) i–V characteristic of the cell and b) power versus current.

Table 2. Cell performance at maximum efficiency (at \(P_{pp}\)) at characteristic external load during illumination.

| Time [\(\text{min}\)] | Current [mA cm\(^{-2}\)] | Potential [V] | Power [mW cm\(^{-2}\)] |
|------------------------|---------------------------|---------------|-------------------------|
| 0                      | 21.75                     | 0.501         | 10.89                   |
| 3                      | 22.50                     | 0.490         | 11.02                   |
| 6                      | 22.50                     | 0.490         | 11.02                   |
| 9                      | 23.25                     | 0.501         | 11.64                   |
| 12                     | 23.25                     | 0.501         | 11.64                   |
| 15                     | 23.25                     | 0.501         | 11.64                   |
| 18                     | 23.62                     | 0.505         | 11.90                   |
| 21                     | 23.62                     | 0.505         | 11.90                   |
| 24                     | 24.00                     | 0.508         | 12.19                   |
| 27                     | 24.00                     | 0.508         | 12.19                   |
| 30                     | 24.00                     | 0.507         | 12.16                   |
| 33                     | 24.00                     | 0.504         | 12.09                   |
| 36                     | 24.00                     | 0.503         | 12.07                   |
| 39                     | 24.00                     | 0.500         | 12.00                   |
| 42                     | 24.00                     | 0.500         | 12.00                   |
| 45                     | 24.00                     | 0.500         | 12.00                   |
| 48                     | 23.62                     | 0.493         | 11.64                   |
| 51                     | 23.62                     | 0.489         | 11.55                   |
| 54                     | 23.43                     | 0.486         | 11.38                   |
| 57                     | 23.25                     | 0.484         | 11.25                   |
| 60                     | 23.25                     | 0.482         | 11.20                   |
| 63                     | 23.25                     | 0.479         | 11.13                   |
| 66                     | 23.25                     | 0.478         | 11.11                   |
| 69                     | 23.25                     | 0.478         | 11.11                   |
| 72                     | 23.25                     | 0.477         | 11.09                   |
| 75                     | 23.17                     | 0.475         | 11.00                   |
| 78                     | 23.06                     | 0.473         | 10.90                   |
| 81                     | 22.95                     | 0.473         | 10.85                   |
| 84                     | 22.87                     | 0.472         | 10.79                   |
| 87                     | 22.87                     | 0.469         | 10.72                   |
| 90                     | 22.87                     | 0.469         | 10.72                   |
| 93                     | 22.87                     | 0.469         | 10.72                   |
| 96                     | 23.06                     | 0.471         | 10.86                   |
| 99                     | 22.87                     | 0.468         | 10.70                   |
| 102                    | 22.68                     | 0.464         | 10.52                   |
| 105                    | 22.68                     | 0.463         | 10.50                   |
| 108                    | 22.68                     | 0.464         | 10.52                   |
| 111                    | 22.68                     | 0.464         | 10.52                   |
| 114                    | 22.68                     | 0.464         | 10.52                   |
| 117                    | 22.68                     | 0.463         | 10.50                   |
| 120                    | 22.68                     | 0.464         | 10.52                   |

\(^{a}\)In natural sunlight for 2 mL of aqueous spinach extract, 9 mL of M/100 Fructose, 6 mL of M/10 NaLS, 15 mL of 1 L NaOH, 3 mL of single distilled water (total volume of solution 35 mL), and Pt of 0.08 cm\(^{-2}\). 
presence of cosensitizers such as carotenoids in crude extract, facilitation of stability and absorbance of chlorophyll by pigments such as carotenoids, etc. This stable and steady-state performance of spinach extract-based PG cell makes it a potential candidate for the solar energy conversion with additional advantage of power storage and sustainability. It can be explained as a steady state, which is a condition or state of a process or system that do not change in time broadly. Steady state may also be described as a condition that changes only negligibly over a specified time. The PG cells are based on the photoelectrochemistry. In chemistry, a steady state is a broader and general situation than a dynamic equilibrium. The dynamic equilibrium is characterized by two or more reversible processes occurring at the same rate. But, in chemistry, a steady state is not necessarily be in a state of dynamic equilibrium, as some of the irreversible processes may also be involved (in a state of dynamic equilibrium). In the present study, for over 2 h, the magnitude of the observed current, potential, power, and efficiency remained nearly the same that is in a steady state. Therefore, the crude spinach extract (a natural, renewable, and sustainable source) has promise for the future for harvesting solar energy at a steady-state rate with power storage capacity as well.

### 3.3. Study on Power Storage Capacity of the PG Cell

Power storage capacity of the cell means the ability to store solar power in sunlight and release that stored power in the absence of sunlight. The electrical performance of the PG cell has been studied in the dark at a peculiar external load resistance of 322.2 Ω, because at this load, the maximum power is extractable from the cell. With the passage of time, the magnitude of the extractable power from the cell goes down due to the deactivation of photosensitizer molecules in dark (Table 3, and Figure 4 and 5). The maximum power extractable at peculiar external load resistance goes down to its half value during the time period (this time period called half-change time $t_{0.5}$). In the present study at cell fabrication parameters as mentioned in the first para of Section 3 of this manuscript, the storage capacity in terms of the half-change time has been observed as 77 min. Even after the half-change time, the PG cell goes on supplying electrical power until the complete discharge of the cell electrically. The PG cell does not show the release of the electrical power for infinite time, as electroactive species (excited sensitizer molecules, semi- or leuco forms of the sensitzers) do not have infinite average lifetime. During charging in the presence of illuminating source and discharging of the cell in the absence of the illuminating source, the PG cell can be charged and discharged as many as times.

### Table 3. Change of power with time (cell performance at maximum efficiency at $P_{pp}$ at characteristic external load in dark).

| Time [min] | Current [mA cm$^{-2}$] | Potential [V] | Power [mW cm$^{-2}$] |
|-----------|------------------------|--------------|----------------------|
| 0         | 22.50                  | 0.580        | 13.05                |
| 10        | 21.25                  | 0.540        | 11.47                |
| 20        | 20.62                  | 0.519        | 10.70                |
| 30        | 19.06                  | 0.492        | 9.37                 |
| 40        | 18.12                  | 0.447        | 8.10                 |
| 50        | 17.81                  | 0.443        | 7.89                 |
| 60        | 17.18                  | 0.433        | 7.44                 |
| 70        | 16.87                  | 0.421        | 7.10                 |
| 77        | 15.93                  | 0.408        | 6.50 ($t_{0.5}$ of 44 min) |
| 85        | 15.00                  | 0.400        | 6.00                 |

### Figure 3. Cell performance at maximum efficiency (at $P_{pp}$) at characteristic external load during illumination (see Table 2): a) potential versus time, b) power versus time, and c) current versus time.

### Figure 4. Cell performance at maximum efficiency (at $P_{pp}$) at characteristic external load in dark (see Table 3): a) power versus time and b) current versus time.

### Figure 5. $i$–$V$ curve in dark after charging of the cell.
source, the observed photopotential is negative, as photosensitizer molecules shed electrons to the working platinum electrode. It shows that the redox potential of the photosensitizer is negative in nature.

### 3.4. Study of Variation of Amount (Volume) of the Crude Aqueous Spinach Extracts (Photosensitizer’s Concentration)

At the optimum amount (volume) of the extract of the leaves of spinach (i.e., 4 mL), the electrical performance of the PG cell was observed optimized in the form of cell parameters such as $i_{sc}$, $P_{pp}$, and CE (Table 4). The cause of that may be the availability of the less number of photosensitizer molecules, at concentration lower than the optimal concentration of the sensitizer, for absorbing photons and, in turn, to give electrons to the anodic platinum electrode in the illuminated chamber. Only the photoexcited sensitizer molecules close to the platinum electrode are, within their exciting lifetime, able to reach the platinum electrode. Sensitizer concentration higher than the optimal concentration will not allow the sufficient number of the photons to reach near the working electrode (Pt) directing to the photoexcitation of reduced number of the sensitizers’ molecules resulting in reduced cell power.

#### 3.5. Study of the Effect of Variation of Reductant’s Concentrations

The electrical performance of the PG cell was found optimized at the optimum concentration (i.e., $2.35 \times 10^{-3}$ M) of reductant (Table 5). At lower reductant concentration ($<2.35 \times 10^{-3}$ M), the performance of the PG cell decreases due to the reduced number of the photons reaching near the working electrode (Pt). The decrease in the number of photons reaching the working electrode (Pt) is due to the reduced number of the photons absorbed by the photosensitizer molecules.

### Table 4. Effect of variation of photosensitizer (volume of crude spinach extract).

| Volume of crude spinach extract | $V_{dark}$ [V] | $V_{max}$ [V] | $V_{oc}$ [V] | $\Delta V$ [V] | $i_{max}$ [mA cm$^{-2}$] | $i_{eq}$ or $i_{sc}$ [mA cm$^{-2}$] | $P_{pp}$ [mW cm$^{-2}$] | $t_{0.5}$ [min] | CE [%] | FF |
|-------------------------------|----------------|---------------|--------------|---------------|------------------------|-------------------------------|-------------------|-----------|-------|---|
| 3.0                           | 0.600          | 1.073         | 1.067        | 0.473         | 53.12                  | 44.37                        | 12.09             | 0.255     | 12.09 | 0.255 |
| 3.2                           | 0.623          | 1.061         | 1.056        | 0.438         | 50.00                  | 48.12                        | 12.47             | 0.245     | 12.47 | 0.245 |
| 3.8                           | 0.547          | 1.095         | 1.088        | 0.438         | 68.75                  | 50.00                        | 13.05             | 0.239     | 13.05 | 0.239 |
| 4.0                           | 0.568          | 1.090         | 1.081        | 0.522         | 69.37                  | 53.12                        | 13.19             | 0.229     | 13.19 | 0.229 |
| 4.4                           | 0.596          | 1.079         | 1.067        | 0.483         | 58.75                  | 53.12                        | 12.77             | 0.251     | 12.77 | 0.251 |
| 4.8                           | 0.611          | 1.060         | 1.058        | 0.449         | 58.75                  | 53.12                        | 12.06             | 0.257     | 12.06 | 0.257 |

Note: At (fructose) = $2.35 \times 10^{-3}$ M, (NaLS) = $1.47 \times 10^{-2}$ M, Temp. = 310 K, Pt electrode area = $0.4 \times 0.2$ cm$^2$, natural sunlight intensity = 100 mW cm$^{-2}$, diffusion length ($D_L$) = 6.3 cm, and pH = 13.72.

### Table 5. Effect of variation of fructose (reductant) concentration.

| (Fructose concentration) $\times 10^{-3}$ M | $V_{dark}$ [V] | $V_{max}$ [V] | $V_{oc}$ [V] | $\Delta V$ [V] | $i_{max}$ [mA cm$^{-2}$] | $i_{eq}$ or $i_{sc}$ [mA cm$^{-2}$] | $P_{pp}$ [mW cm$^{-2}$] | $t_{0.5}$ [min] | CE [%] | FF |
|-------------------------------------------|----------------|---------------|--------------|---------------|------------------------|-------------------------------|-------------------|-----------|-------|---|
| 1.47                                      | 0.643          | 1.040         | 1.032        | 0.397         | 53.12                  | 44.37                        | 12.09             | 0.255     | 12.09 | 0.255 |
| 1.78                                      | 0.681          | 1.061         | 1.057        | 0.380         | 50.00                  | 48.12                        | 12.47             | 0.245     | 12.47 | 0.245 |
| 2.05                                      | 0.563          | 1.053         | 1.042        | 0.490         | 61.25                  | 50.00                        | 13.05             | 0.239     | 13.05 | 0.239 |
| 2.35                                      | 0.547          | 1.095         | 1.088        | 0.548         | 68.75                  | 53.12                        | 13.19             | 0.229     | 13.19 | 0.229 |
| 2.50                                      | 0.522          | 1.081         | 1.077        | 0.559         | 63.75                  | 53.12                        | 12.77             | 0.251     | 12.77 | 0.251 |
| 2.64                                      | 0.567          | 1.083         | 1.072        | 0.516         | 66.25                  | 53.12                        | 12.06             | 0.257     | 12.06 | 0.257 |

Note: At crude spinach extract = 3.8 mL, (NaLS) = $1.47 \times 10^{-2}$ M, Temp. = 310 K, Pt electrode area = $0.4 \times 0.2$ cm$^2$, natural sunlight intensity = 100 mW cm$^{-2}$, diffusion length ($D_L$) = 6.3 cm, and pH = 13.72.
the available reductant molecules are less in number to cause reduction of reduced numbers of sensitizers’ molecules. In turn, the number of available reduced sensitizer molecules transferring electron to platinum electrode may be few in number leading to low cell power. Higher concentration (>2.35 \times 10^{-3} \text{ M}) of the reductant will hinder propagation of photons and diffusion of excited sensitizer molecules toward the platinum electrode leading to the lower cell power. NaLS is not able to absorb in visible range, but it has been found to absorb up to 340 nm in the UV region, although it is not an electroactive species.\textsuperscript{409} There are many sensitizers present in the crude extract that absorbs in the UV region. Therefore, we perceive that a very high concentration of reductant (fructose) will lower the prospect of absorption of the sunlight by crude aqueous extract. Furthermore, a higher concentration of fructose reductant will also augment the back electron transfer process (electron transfer from semi/leuco forms of the sensitizer molecule to reductant molecule).\textsuperscript{406} Also, in addition to this, the current is also unfavorably influenced by the higher concentration of the reductant, because the incident photons are made to be absorbed at a position in the electrolyte that is too far away from the illuminated platinum working electrode for the photogenerated semi/leuco forms of the sensitizer molecules to reach it before decomposing.\textsuperscript{409}

3.6. Effect of Variation of Surfactant (NaLS) Concentration

The electrical performance of the PG cell was observed optimal at the optimum concentration of the surface-active reagent NaLS (i.e., 1.47 \times 10^{-2} \text{ M}) (Table 6). Reason is that at lower concentration (<1.47 \times 10^{-2} \text{ M}), the number of available surfactant molecules is less in number, leading to few electron transfer and reduced dissolvability and photostability of the photosensitizer. The higher concentration (concentration >1.47 \times 10^{-2} \text{ M}) of the surfactant will inhibit propagation of photons and diffusion of excited sensitizer molecules toward the platinum electrode leading to the lower cell power. NaLS is not able to absorb in visible range, but it has been found to absorb in the UV region (\lambda_{\text{max}} of 260 nm and A_{\text{max}} of 0.04 in water). There are many sensitizers present in the crude extract that absorbs in the UV region. Therefore, we perceive that the very high amount (concentration) of the surface-active reagent NaLS will lower the possibility of absorption of the sunlight by the aqueous crude extract of the leaves of the spinach vegetable.

3.7. Effect of Variation of pH

At the optimum amount of pH (i.e., 13.69), the electrical performance of the PG cell was optimal (Table 7). The electrical performance of the PG cell may be low at low value of pH owing to 1) higher proton concentration favors proton’s preferential cathodic reduction to the hydrogen; 2) proton attachment to the lone pairs/unsaturated bonds of the molecules of the photosensitizer (chlorophyll) and molecules of the fructose reductant directing to the low electron-donating power of reductant molecule to the photosensitizer and that of photosensitizer to Pt electrode; 3) lack of anionic form of chlorophyll; 4) pheophytinization; 5) higher decolorization of sensitizer material; and 6) emergence of the turbidity at lower value of the pH.

The chlorophyll “a” molecule may also behave as an electron donator via its ring “E” and keto carbonyl groups existing in the ring and side chains,\textsuperscript{411} leading to the increased protonation of the chlorophyll sensitizer molecules at lower pH with its decreased electron-donating tendency to the platinum electrode (see Scheme 1). It may be explained, as the higher density of electrons in an entity increases the electron-donating tendency of that entity. In “E” ring of chlorophyll “a” molecule, the oxygen atom of the carbonyl group of ketone group and ester group bears the lone pairs of electrons. At low pH, a higher concentration of the H\textsuperscript{+} will favor increased protonation (through the lone pairs of electrons) of the oxygen atom of the carbonyl group of ketone

\[ \text{Table 6. Effect of variation of NaLS (surfactant) concentration.} \]

| Cell parameters \textsuperscript{a} | (NaLS concentration) \times 10^{-2} \text{ M} |
|-----------------------------------|----------------------------------|
|                                   | 0.58                             | 0.88                             | 1.17                             | 1.47                             | 1.61                             | 1.76                             |
| \( V_{\text{dark}} [V] \)          | 0.569                           | 0.502                           | 0.693                           | 0.547                           | 0.704                           | 0.459                           |
| \( V_{\text{oc}} [V] \)            | 1.110                           | 1.100                           | 1.106                           | 1.095                           | 1.097                           | 1.109                           |
| \( V_{\text{max}} [V] \)           | 1.107                           | 1.100                           | 1.098                           | 1.088                           | 1.093                           | 1.102                           |
| \( \Delta V [V] \)                 | 0.541                           | 0.598                           | 0.413                           | 0.548                           | 0.393                           | 0.650                           |
| \( t [\text{min}] \)               | 10                              | 22                              | 17                               | 13                               | 18                              | 16                              |
| \( i_{\text{max}} \text{[mA cm}^{-2}] \) | 18.12                           | 53.75                           | 61.87                           | 68.75                           | 61.25                           | 58.75                           |
| \( i_{\text{max}} \text{ or } i_{\text{oc}} \text{[mA cm}^{-2}] \) | 42.50                           | 53.12                           | 46.25                           | 50.00                           | 49.37                           | 46.87                           |
| \( P_{\text{sp}} \text{[mW cm}^{-2}] \) | 12.03                           | 12.24                           | 12.64                           | 13.05                           | 12.92                           | 12.83                           |
| \( t_{\text{fl}} \text{[min]} \)   | 18                              | 45                              | 31                               | 77                               | 85                              | 27                              |
| \( \%CE \text{[\%]} \)            | 12.03                           | 12.24                           | 12.6                            | 13.05                           | 12.92                           | 12.8                            |
| \( FF \)                           | 0.255                           | 0.258                           | 0.248                           | 0.239                           | 0.239                           | 0.248                           |

\textsuperscript{a}At (fructose) = 2.35 \times 10^{-3} \text{ M}, crude spinach extract = 3.8 mL, Temp. = 310 K, Pt electrode area = 0.4 \times 0.2 \text{ cm}^2, natural sunlight intensity = 100 mW \text{ cm}^{-2}, diffusion length (D_L) = 100 \text{ cm}, and pH = 13.72.
At low pH, the prosthetic group (i.e., cofactor chlorophyll) is removed at a very slow rate. At very high pH, and in high pH solutions (alkaline solutions), this process of chlorophyll molecule, converting it to the pheophytin molecule, will decrease the electron density in the chlorophyll molecule, providing suitability of orientation for one or both Mg axial positions to be coordinated with a molecule having a lone electron pair capable of behaving as an electron donor. Therefore, we view that intactness of Mg with chlorophyll facilitates electron transfer from reductant to chlorophyll and, in turn, from chlorophyll to Pt. On the removal of the Mg during pheophytinization, this property of electron transfer is lost, and the efficiency of cell is reduced.

Metalloporphyrins such as chlorophylls are electrochemically active, and their high stability allows redox reactions to proceed under severe conditions. The increased solubility of metalloporphyrins at higher pH favors them electrochemically. At higher pH, the reducing property of reductant is also high. The higher pH may disfavor the regeneration of the original form of the reductant molecule, leading to the reduced solar cell electrical output.

### 3.8. Study of Effect of Variation of Diffusion Length on the Cell Performance

Inside the bulk of the electrolyte, the ions are current carriers in the PG cells. Therefore, the efficiency of these cells is limited by diffusion capacity of the ions. In the mechanistic view of the photogeneration of current in these cells, the photoexcited sensitizer molecules must reach within their exciting lifetime to the platinum electrode. Therefore, the diffusion length \(D_L\) is one of the determining factors affecting the efficiency of the cell. At the optimum value of the diffusion length, the electrical performance of the cell was observed as optimal. At higher value of diffusion length \(D_L\), the photocurrent may rise as a result of increased conductivity due to large amount of the volume of electrolyte solution between the two electrodes. Contrary to it, the higher diffusion length may disfavor potential as a result of

![Scheme 1. Structure of chlorophyll.](Image)
higher concentration gradient. The $D_e$ of the excited species is not 4 cm. The diffusion length is the distance between electrodes in PG[15] cell, and in my case, it is the distance between the centers of two arms of H-shaped glass tube. Therefore, we do not say that excited chlorophyll has a diffusion length of 4 cm and diffuses from one electrode to another.

3.9. Study of Effect of Variation of Platinum (Pt) Electrode Area on the Cell Performance

At the optimum dimension (area) of the Pt working electrode, the electrical performance of the PG cell was observed as an optimal performance. For the studied dimensions (area) of the platinum working electrode, the maximum current, equilibrium current, power at power point, solar energy CE, and half-change time were observed optimally highest for the platinum electrode of dimension $0.40 \times 0.20 \text{ cm}^2$. Under the study on selected Pt electrode dimension (area), the best electrical performance of the PG cell was observed with minor-sized platinum electrodes. Reason for it may be the reduced obstacle in the diffusion of the ions in bulk electrolyte. The reduced hindrance in ion diffusion facilitates higher cell power, as these cells are diffusion-controlled devices. Therefore, we consider our results noteworthy as we have accomplished relatively higher level of electrical performance of the PG cell using small-sized platinum electrode (less cost) in comparison with the already published work on the PG cells (earlier cells exploited only large-sized Pt electrodes).[13,15]

Thus, the exploitation of small-sized platinum electrodes will increase economic and environmental competitiveness of these cells.

3.10. Originality of the Present Manuscript Especially with Respect to Earlier Reported Study (Environ. Prog. Sustain. Energy)[19]

The originality of the present manuscript especially with respect to earlier reported study[19] is justified as only some points. Every solar cell technique has to show its workability in natural sunlight. Only then that solar cell technique can have applied significance to meet energy needs of the society. In the present study, the cell performance is shown in natural sunlight conditions ultimately for daily life needs of the society. In the previous study,[19] the work was studied in laboratory conditions of artificial and low intensity.

See Table 2 and Figure 2 showing originality in respect of stability and long-term use of PG cells in natural light. In the present study, authors have noted similar and repetitive cell performance by charging similar PG cells on different days in natural sunlight. The results of different times are the same or negligibly different. This aspect of experimentation was not part of the previous study.[19]

The exposed area of the solution that is small or large shows the same phenomenon such as current, etc. This fact has been studied in the present work, but not in earlier work.[19] For a study at different illumination window sizes, each cell has used a natural sunlight intensity of 100 mW cm$^{-2}$, a diffusion length ($D_e$) of 6.3 cm, a Pt electrode area (0.4 × 0.2 cm$^2$), 3.8 mL of crude spinach extract, 36 mL of NaOH (pH 13.72), 16 mL of M/100 fructose (resultant concentration of 2.35 × 10$^{-3}$ M), and 10 mL of M/10 NaLS (resultant concentration of 1.47 × 10$^{-2}$ M). The cells were illuminated through the window sizes of 2.0 × 1.5 cm$^2$ (3.0 cm$^2$), 1.5 × 0.8 cm$^2$ (2.0 cm$^2$), 0.8 × 0.6 cm$^2$ (0.48 cm$^2$), 1.0 × 1.0 cm$^2$ (1.0 cm$^2$), and 0.4 × 0.2 cm$^2$ (0.08 cm$^2$), respectively (Table 8).

3.11. Light Intensity and Incident Angle for Illuminating the Cell in Present Study

A concern has been raised on this work that the authors tried to test devices under natural sunlight outside. However, there are no standards used. The conditions such as light intensity and incident angle must be different depending on the weather and time. Therefore, the authors have to show the detailed conditions for testing.[4]

For the present study involving experiment having highest power, the sunlight incident angle was 88°–84.75°, and the light intensity was ≈97.18 mW cm$^{-2}$. The cell was charged for 13 min from the local time 12:48 AN-1:01AN (i.e., incident angle of 88°–84.75°).

Table 8. Study at different illumination window sizes.

| Cell parameters\(^{a,b}\) | Illumination window size |
|--------------------------|-------------------------|
|                          | 2.0 × 1.5 cm$^2$ | 1.5 × 0.8 cm$^2$ | 1 × 1 cm$^2$ | 0.8 × 0.6 cm$^2$ | 0.4 × 0.2 cm$^2$ |
| $V_{dark}$ [V]           | 0.717              | 0.717              | 0.715          | 0.711              | 0.712              |
| $V_{max}$ [V]            | 1.070              | 1.077              | 1.079          | 1.070              | 1.076              |
| $V_{eq}$ [V]             | 1.064              | 1.072              | 1.074          | 1.066              | 1.073              |
| Jump time [min]\(^{b}\) | 5                  | 4                  | 4              | 3                  | 4                  |
| Cell illuminated for time [min] | 32              | 32                  | 32             | 32                  | 32                  |
| $i_{max}$ [$\mu$A]       | 6200               | 6200               | 6200           | 6200               | 6200               |
| $i_{eq}$ [$\mu$A]        | 3900               | 3900               | 3900           | 3900               | 3900               |
| $P_{pp}$ [kW]            | 1039.6             | 1039.4             | 1039.4         | 1039.6             | 1039.5             |

\(^a\) At (fructose) = 2.35 × 10$^{-3}$ M, crude spinach extract = 3.8 mL, Pt electrode area = 0.4 × 0.2 cm$^2$, natural sunlight intensity = 100 mW cm$^{-2}$, diffusion length ($D_e$) = 6.3 cm, and pH = 13.72; \(^b\) Time in which potential rises abruptly.
This part of the concern is addressed in the present study, and the facts mentioned in manuscript are also supported by the published study. The conditions such as light intensity and incident angle do not affect PG cells, as these cells use dye sensitizers, and dye sensitizers are also capable of photoexcitation in even low and diffused sun intensity. This fact is also supported by the fact that the DSSCs also work in low light operating conditions due to their workability in such conditions and their weaker dependence on the angle of light incidence. The ultimate aim of solar research is to develop solar cells capable of solar power generation and storage in natural daily life conditions (uncontrolled) to meet energy needs of the society. The workable feasibility of the solar cells in laboratory conditions is not sufficient. Here, in the present study, the results are reported for daily life conditions consistent with the ultimate aim of the solar cells. The experiment has been done in natural environment (outside the laboratory) conditions in day time during natural sunlight. The cell was placed facing the sunlight direction. The experiment was done in Jodhpur, which receives the second highest sun intensity in the world. The sky in Jodhpur remains clear, and that was also during the experiments. Therefore, the sun intensity as measured and stroked with cell was of average value.

3.12. Photostability of Various Fabrication Parts of the PG Cell

A fabricated PG cell has parts such as H-glass tube, platinum electrode, combination electrode, chlorophyll “a” sensitizer, fructose, sodium lauryl sulfate, and sodium hydroxide. The PG cell device is illuminated with the sunlight. Therefore, the photostability of various parts of the cell is of utmost importance. Some parts of the cell such as H-glass tube, platinum electrode, and combination electrode are robust in nature as far as their photostability is concerned. Furthermore, the sunlight reaching the Earth’s surface (i.e., the surface of the solar cell) primarily consists of the visible and IR radiations, and UV component reaching the Earth is quite negligible. The fructose ($\lambda_{\text{max}} \approx 240 \text{ nm}$), sodium lauryl sulfate ($\lambda_{\text{max}} \approx 200 \text{ nm}$), and sodium hydroxide ($\lambda_{\text{max}} \approx 200 \text{ nm}$) components of the cell show electron transition absorption spectra in the UV region. Therefore, these chemicals (fructose, sodium lauryl sulfate, and sodium hydroxide) are impervious to photodecay in the visible and IR region. But, contrary to all other parts of the cell, the dye photosensitizers are prone to photodecay in the visible region, because the sensitizer molecule absorbs the visible light for electronic transition. But, the natural photosensitizers as chlorophyll “a” used in the present study are quite less prone to photodecay in comparison with the photodecay of the synthetic dyes. The natural photosensitizers as used in the present work offer some more additional benefits such as higher photostability and rejuvenation as in the photosynthesis process owing to extended II-framework and tetra pyrrole macrocyclic ring framework (nine conjugated double bonds that is 18 pie electrons optimal length), whereas the artificial and laboratory-synthesized dye materials are thermally degraded and lack rejuvenation power, as their II-frame is not so extensive. Such an extensively large optical length of a tetra pyrrole nucleus structure of chlorophyll facilitates greater photoexcited state stability, leading to the greater electrical cell performance.

The cell parameters of this cell charged in sunlight (of artificial and low intensity, i.e., $10.4 \text{ mW cm}^{-2}$) as reported in the previous study are summarized as a $V_{\text{max}}$ of 1.056 V; a $V_{\text{oc}}$ of 1.050 V; a $t$ of 18 min; an $i_{\text{max}}$ of 2.4 mA; an $i_{\text{sc}}$ of 1.75 mA; a $P_{\text{pp}}$ of 0.384 mW; an $i_{\text{pp}}$ (current at $P_{\text{pp}}$) of 800 $\mu$A; a $P_{\text{pp}}$ of 480 mV; a $t_{0.5}$ (half-change time) of 44 min; a CE of 9.22%; and an FF of 0.20.

The electrical parameters of the PG cell in the present study at natural illumination intensity ($\approx 100 \text{ mW cm}^{-2}$) in the present study are summarized as a $V_{\text{max}}$ of 1.095 V; a $V_{\text{oc}}$ of 1.088 V; a $t$ of 13 min; an $i_{\text{max}}$ of 5.5 mA; an $i_{\text{sc}}$ or $i_{\text{oc}}$ of 4.0 mA; a $P_{\text{pp}}$ of 1.044 mW; a $t_{0.5}$ of 77 min; a CE of $\approx$13%; and an FF of 0.23. We see that the results of the present study on use of crude spinach extract are nearly 2–3 times higher in natural sunlight ($\approx100 \text{ mW cm}^{-2}$) than that in artificial light ($10.4 \text{ mW cm}^{-2}$).

Thus, we perceive that the aqueous crude extract (of the leaves of spinach) is capable of photosensitizing PGs for the harvesting of solar energy with storage facility as well. The aqueous crude spinach extract photosensitized PG cells also obey the similar propositions as applicable for synthetic and artificial dye photosensitized PG solar cells. The cell fabrication parameters (physical parameters such as temperature, diffusion length, platinum electrode area, cathodic electrode, cell vessel size and shape, etc.) and chemical parameters (such as variety and amount of the light-absorbing materials, reducing agents, surface-active reagents, alkali, etc.) are limiting variables affecting the cell performance. The optimum electrical performance of the PG cell can only be attained by correctly choosing the best possible magnitude of all these cell fabrication variables. It has also been observed that the use of a larger volume of solution (but the same resultant concentration) does not give proportionally higher current and power. The reason may be that higher resistance resulting from the larger volume of solution offsets the efficiency and electrical power yield of the PG cell.

Authors have noted similar and repetitive cell performance by charging similar PG cells on different days in natural sunlight. The results of different times are the same or negligibly different.

The exposed area of the solution that is small or large shows the same phenomenon such as current, etc. Also, the Pt electrode area affects the results such as current, etc. Therefore, the main electrical cell parameters such as current and power have been normalized to the size of the platinum working electrode.

The fundamental principles (such as electrochemical measurements for reversibility) of PG cells are already established by researchers. Therefore, the electrochemical measurements of the sensitizer and Fructose have not been done in this work, because this aspect of reductant and sensitizer is already extensively studied. The PG cell has dual functionality of conversion and storage. But, the PG is not like bio-fuel cell, as no fuel (chemical) is consumed in PG, whereas fuel is consumed in bio-fuel cell.

3.13. Role of Electrodes in the PG Cell

Here, in this article and also all published papers on PG cells, the illuminated electrode (i.e., Pt) is a working electrode, and the
dark electrode (i.e., SCE) is a reference electrode. The higher current is not due to SCE in this article. Had SCE been reason for higher current? Then, $i_{sc}$ current would have been higher in all PG using SCE. As in DSSC, the dark chamber electrode SCE is supposed to work as a counter electrode to regenerate the electrolyte. Photogenerated electrons from dye are transferred through the oxidized electrolyte diffusing toward the electrode in the nonilluminated cell region. The task of electrode in the nonilluminated cell region is to transport the electron that arrives through the external wiring (circuit) step back to the redox electrolyte system.

3.14. Bandgap of Chlorophyll Sensitizer, Theoretically Calculated Current, and Efficiency

The efficiency of $\approx 13\%$ is justified on theoretical current and observed current basis also.

There is no doubt on observed absolute current 4000 $\mu$A in the present study, as the same is readable in ammeter. Furthermore, one of the authors has observed even higher currents in natural sunlight as reported in the Journal of Power Sources. From basic concepts, the current reported in the present manuscript is also explainable. Chlorophyll sensitizer is characterized by a bandgap energy close to 2 eV. There is no doubt about the current ($4000 \mu$A) and the current density (50 mA cm$^{-2}$ with respect to the Pt area) in this article, as we have experimentally observed it. Also, the observed result (current) is also consistent with the theoretical calculation. Using an average sun intensity of 100 mW cm$^{-2}$, at 440 nm absorption band of chlorophyll “a” (absorbance 1.65 and absorbed intensity 97.7% in the presence of electrolyte), the calculated current density comes 34.3 mA cm$^{-2}$. If the sun intensity considered is 140 mW cm$^{-2}$, then the calculated current density is 78.2 mA cm$^{-2}$ (with respect to Pt electrode), and the calculated current is 6258 $\mu$A.

Author does not have the incident photon conversion efficiency (IPCE) facility, although it should have added more credence to the reported results. But, the concept of current at monochromatic light in laboratory is subdued in natural polychromatic light. For ultimate significance of the solar cells, their study in natural polychromatic light is of importance, and that has been shown in the present manuscript.

3.15. Present Study Promising for PG Cells

World over, the PG cells have been condemned for lower value of electrical output and, in turn, for practical inapplicability. In the present study, the electrical output so achieved is not only impressive among PG cells published so far, but also equivalent to the commercial inorganic solar cells. Contrary to earlier researcher of 1970s, we view that the PG cells are efficient and capable of showing high CE as forecasted by Albery et al. that the efficiency of PG cells could be as high as 18%. Therefore, the low cost and inherent power storage capacity of these cells, which is their edge over inorganic solar cells, need to be exploited. Here, the use of Pt and SCE is less costly and less polluting in the sense that they are not consumed during power generation through PG cells, and they are reused in PG cells.

The fructose in this article is cheap in the sense that its 16 mL of M/100 molar solution has been used, and the obtained result is very high ($i_{sc}$ of 4000 $\mu$A and $P_{pp}$ of 1044 $\mu$W). The EDTA, ascorbic acid, and D-xylose have reported very low result, and preparing the same molar solution (16 mL of M/100) will cost more. With extra advantage of storage capacity coupled with low cost and more eco-friendliness, the bio-materials such as spinach extract-based PG cells have the promise to yield the solar power equivalent to that generated from the commercial inorganic solar cells (which yet lacks inherent power storage capacity). The natural photosensitizers as used in the present work offer some more additional benefits such as higher photostability and rejuvenation as in the photosynthesis process owing to extended II-framework and tetra pyrrole macroyclic ring framework (nine conjugated double bonds that is 18 pie electrons optimal length), whereas the artificial and laboratory-synthesized dye materials are thermally degraded and lack rejuvenation power, as their II-frame is not so extensive. Such an extensively large optical length of a tetra pyrrole nucleus structure of chlorophyll facilitates greater photoexcited state stability, leading to the greater electrical cell performance.

We report the use of photosensitizers present as such in the easily accessible aqueous crude extract of the green leaves of the spinach vegetable for harnessing solar energy for the electricity generation and storage. The work described in this manuscript does not require any separation/isolation/extraction/laboratory manufacturing of the molecules of natural occurring photosensitizers, or mastery of surface chemistries, or deposition of thin films, or photoillumination with sunlight having narrowing range of wavelengths.

This way, the study in this manuscript describes a very easy, uncomplicated, and cheap method of exploiting the natural photosensitizers in natural sunlight for harnessing the solar energy with storage having additional benefit of very high electrical output over light harvesting by already published work on isolated natural sensitizers. The experimentally noted open-circuit potential and CE in the present work are either higher or comparable, and short-circuit current and maximum power are very high for aqueous crude spinach extract than that for the already published work on isolated natural sensitizers. The open-circuit potential value for aqueous crude extract is comparable to that of Photosystem-I (PSI) donor–acceptor sides ($\approx 1$ V).

The observations of Bolton and Hall and one of the reviewers that the theoretical maximum efficiency for the conversion of solar energy into chemical energy by plant-type photosynthesis is 13%. The plant-type photosynthesis is the same as the photochemical process of the PG cell being described in this article. The theoretical maximum efficiency, i.e., 13% value of a PG cell device based on the use of chlorophyll as the photosensitizer vindicates 13% efficiency as reported in this article.

One of the concerns in this work is the solar energy conversion with simultaneous storage facility. On this aspect, it demonstrates quite good photostability of aqueous crude spinach extract photosensitized PG solar cell devices vis-à-vis that of the isolated natural photosynthetic protein-molecular complexes in solid-state phase devices. It is pertinent to mention here that the availability of crude extract can be achieved in a very simple and cheap manner, whereas the isolation and extraction of the natural pigments are very complex and costly affair.
Therefore, the importance of these simplified PG cell devices based on aqueous crude spinach extract lies in their tremendous stability associated with the higher open-circuit potential, efficiency, power output, and inherent power storage capacity. Spinach extract is a good alternative for synthetic dyes in PG cells. The PG cell performance depends on many factors such as sensitizers’ chemical and physical structures (stability, solubility, aggregation, etc.). The observations and explanations as described in the present work are also supported by previously published studies as listed in succeeding paras.

The separation and use of the pure chlorophyll shall be costly, polluting, and useless. The separation of pure chlorophyll will need polluting costly and inflammable solvents such as alcohol or acetone and ether. The pure chlorophyll is insoluble in the water. The solubility aspect of natural pigments in the water has been taken care of using surfactant, which not only helps in solubilization, but also in mitigating aggregation of sensitizer. Therefore, the use of pure chlorophyll in the cell will need alcohol or acetone or ether for solubility of chlorophyll. Also, the use of pure chlorophyll will not offer any advantages such as power output. Therefore, the use of the crude extract is cheap, eco-friendly, and easy to use. The carotenoids and other pigments provide in vivo such as environment to chlorophyll “a.” The chlorophyll “b,” carotenoids, and other pigments help chlorophyll “a” to exploit the broader spectrum for the solar power generation. The irradiation of chlorophyll solution results in the breakdown of chlorophyll,[57–60] and here, the ancillary pigments (chlorophyll “b,” carotenoids, and other pigments present with the chlorophyll “a”) also help in the photostability of the chlorophyll “a” molecule. Hao et al.[61] have also reported study on chlorophyll present in kelp plants’ extract with good cell efficiency. Hug et al.[24] have also reported that the natural pigments-based cells are very attractive option.

The dye–surfactant interaction leading to the mitigation of dye aggregation affects PG cells favorable. The force of attraction between sensitzer molecule and surfactant is van der Waals forces and hydrophobic in nature. The dipole–dipole interactions between sensitzer molecule and surfactant may be the electrostatic repulsion and attraction (attraction between oppositely charged surface-active reagents and sensitizer dye molecules, and repulsion between similarly charged surfactant molecules and dye molecules). In aqueous spinach extract, the chlorophyll “a” is the main light-absorbing component. Chlorophyll “a” is a neutral metal complex structure having long alkyl chain. This long alkyl chain may be facilitating deaggregation of chlorophyll “a” sensitizer owing to hydrophobic and van der Waals attractive forces between sensitzer molecule and surfactant molecule.[24]

Chlorophyll “a” assists in the formation of anionic micellar aggregates, which are characterized by enhanced optical activity and light absorption with bathochromic and hypochromic shifts.[25] Increased absorption and bathochromic shifts enhance the PG cells’ efficiency. Mall et al.[15] have reported that the surfactant increases the physical properties such as stability and solubility of the photosensitizers, and rise in stability and solubility direct to the enhancement in the power output of the PG cells. Electrical data of the cells based on the dye photosensitizers showing surfactant-induced red shifting in the light absorption due to greater stability in the excited state. Blue shifting causes lowering of the cell electrical data SDS. Mall et al.[15] have reported that the dye molecule-surface-active reagent complex having greater stability in the photoexcited state might be of more value for improving the solar energy CE and also the storage capacity of PG cells in the future.

Hybrid systems (solar battery combined with solar super capacitor) provide for solar power generation and storage. The PG cells alone have inherent power storage capacity simultaneously with the solar power generation. This way, the PG cells are promising and advantageous. See Figure 3 for power storage capacity of PG cells. Figure 3 shows the performance of the PG cells in dark (in the absence of illumination) in which the cell is showing extraction of stored power, which was stored in cell during illumination. The power storage is determined in respect of half-change time ($t_{0.5}$).

Natural pigments have also been extensively studied in the DSSC with conclusion that the efficiency of natural pigments is still lower than that of synthetic pigments. The cited reasons are 1) that the anchoring of natural pigments with TiO2 is relatively less, and anchoring of the molecules (of the synthetic sensitizers) with the TiO2 is relatively greater,[1,2,23,47] and 2) that there is low charge-transfer absorption for natural pigments in the whole visible range.[55] But, here, this cause of concern is not applicable to the PG cells, as sensitizer is used in their bulk electrolyte solution. Therefore, any factor which disperses and stabilizes the sensitizer molecule in the solution shall facilitate electrical data of PG cells. There are the background reports, which point out that the dye stability and solubility pose a main problem in the PGs. In the present manuscript, therefore, the NaLS as a surface-active reagent has been used to tackle these problems.

The presence of sensitizers other than the chlorophyll in the crude spinach extract may also be facilitating the cell efficiency in the present work. It finds support from the reported study on the DSSC that the cosensitization or dye cocktails facilitate higher CEs if the overall absorption spectrum is extended as a result of not too overlapping of the spectra of different sensitizers.[23] The spinach extract in the present study has carotenoids with chlorophyll also. Such combination may also be reason for good efficiency of the PG cell in the present work. It finds support from the published study that using the carotenoids in association with the chlorophyll derivatives can increase efficiency of DSSCs.[22] Ammar et al. have also studied the role of crude filtrate of extract of spinach in DSSC. They have reported that the UV–Visible light absorption spectrum of the chlorophyll pigment separated from the spinach vegetable is characterized by two different absorption peaks (662 and 431 nm). Time-resolved photoluminescence has been reported to show a long lifetime and high short-circuit current for the chlorophyll pigment molecule in comparison with that for the molecule of anthocyanin dyes.[28] The long lifetime indicates reduced recombination rate and increased electron gathering efficiency.[62] The pigments/dyes extracted from the spinach vegetable are mostly chlorophyll molecules and carotenoids (xanthophyll) and carotene. The presence of the oxygen atoms mostly as epoxide and hydroxyl groups in the xanthophylls helps to increase the polarity (of xanthophylls) and also helps to increase the binding property (of xanthophylls) with the TiO2 layer.[63]
75.93% are reported.[24] In another study, for the chlorophyll-sensitized DSSCs, an $\eta$ of 0.30%, an $i_{sc}$ of 0.8 mA cm$^{-2}$, a $V_{oc}$ of 0.56 V, and an FF of 57.93% are reported.[25] For the tereatin-sensitized DSSCs, an $\eta$ of 0.13%, an $i_{sc}$ of 0.3 mA cm$^{-2}$, a $V_{oc}$ of 0.54 V, and an FF 81.82% are reported.[25] For Areca catechu extracted natural sensitizer-based DSSCs, an $\eta$ of 0.118%, an $i_{sc}$ of 0.3 mA cm$^{-2}$, a $V_{oc}$ of 0.536 V, and an FF of 73.5% are reported.[26] A comparison of the results of the present study with the above-mentioned results for the DSSCs shows that the FF for the DSSCs based on anthocyanin sensitizer, tereatin sensitizer, and Areca catechu extracted natural sensitizer is very high. Therefore, for improving the FF of the PG cells, the anthocyanin sensitizer, tereatin sensitizer, and Areca catechu extracted natural sensitizer provide good opportunity in future.

In conclusion, the crude spinach extract provides for low cost, abundant, and sustainable material for harvesting solar electricity with storage facility through the PG cell devices. However, the exploitation of costly and less-abundant Pt and very costly and delicate SCE still poses challenges for economic sustainability of the PG cells. Therefore, the study on use of alternative electrodes is a new area of future research in PGs. In future, some more efficient natural pigments as anthocyanin and tereatin extracted from the flowers of Ixora coccineae[24] and Clitoria ternatea,[25] respectively, may be used in PG cells. A new type of natural organic dye sensitizer derived from the Malaysian Areca catechu (Pinang) fruit[26] may also be the basis for fabricating PG cells.

### 4. Conclusion

We conclude that crude aqueous spinach extract containing natural pigments as such can be used to fabricate the PG cells for harvesting solar electricity with storage facility. The aqueous crude extract of the spinach leaves has been observed equally efficient as synthetic photosensitizers. The use of natural resources as the aqueous crude extract of the leaves of spinach will offer additional advantages of the reduced economic and environmental cost. Crude spinach aqueous extract-based PG cells charged in the natural sunlight follow the similar concepts as applicable to the PG cells based on the artificial and synthetic dye sensitizers charged in the low and artificial illumination intensity. The PG cell is able to perform in a stable and steady manner at maximum power at characteristic external load during the illumination with natural sunlight. Therefore, we conclude that naturally occurring resources such as Spinach—that is a resource as close as nature—provide a good alternative for the artificial and synthetic dye sensitizers for harnessing the solar electricity with storage facility using the PG cell devices in the natural sunlight as well. Furthermore, the study on use of alternative electrodes and alternative pigments such as anthocyanin, tereatin, and natural organic dye sensitizer derived from the Areca catechu (Pinang) fruit is a new area of future research in PGs.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

Research data are not shared.

### Keywords

bio-photogalvanic cells, crude spinach extract, photocatalyzed power, storage capacity

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