Defence Life Science Journal, Vol. 8, No. 2, April 2023, pp. 111-115, DOI : 10.14429/dlsj.8.17920

Exploring Carotenoid from *Rhodococcus Kroppenstedtii* as a Photosensitizer in a Dye-Sensitised Solar Cell

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ABSTRACT

A Dye-Sensitised Solar Cell (DSSC) is a low-cost thin film solar cell that works in diffused light and comes in a variety of colors. Most of the investigations on organic dye-based DSSC have used pigments from flowers and fruits as photosensitizers. With the majority of the world's economy reliant on agriculture to meet the food and feed demand, using agricultural resources for color extraction is not a realistic solution. Alternative dye resources, such as microorganisms, must thus be investigated in DSSCs to ensure a long-term future. The present study was a preliminary investigation to explore the potential of carotenoids derived from an actinobacteria *Rhodococcus kroppenstedtii* as a photosensitizer in a DSSC. The carotenoid extract from *R. kroppenstedtii* was subjected to stability analysis, to ascertain its potential as a photosensitizer. The extract was found to be stable at varying temperatures (0-80 °C), pH (3-11), and light conditions (dark, white light, sunlight), indicating its potential applicability as a photosensitizer. Further, increasing concentrations (12.5 *mg/mL*-100 *mg/mL*) of the extract was used for sensitization of TiO_2 in a DSSC assembly. The extract showed a linear rise in power output (078±0.0001 - 20.75±0.0003 *mW*), which proposes its scope as a stable and cheap photosensitizer in a DSSC.

Keywords: Carotenoids; DSSC; Photosensitizer; *Rhodococcus kroppenstedtii*; Stability

1. INTRODUCTION

The technologically driven world is advancing at a breakneck speed, and with it comes an increase in global energy demand. According to the International Energy Agency's (IEA) energy market analysis, worldwide electricity demand is expected to surge by roughly 2.3 % in 2022-2023. Currently, power plants account for over 30 % of total carbon emissions, which is a major cause of concern for the environment.[2] Solar-powered renewable electricity generation is not only a cost-effective but also an environmentally beneficial way to address the world's growing energy demand.[3] Solar cells can reduce carbon emissions while also reducing reliance on non-renewable resources, and as a result, major economies throughout the world are attempting to develop solar-powered technologies.

Although the conventional silicon-based solar cells have demonstrated high efficiency and stability, their price and disposal limit their deployment.[4] As a result, organic thin film solar cells should be investigated further as a cost-effective and environmentally benign option.[5] Thin film solar cells offer the advantages of being lightweight, easy to install, and cost-effective, but they still need to be improved in terms of energy efficiency.[4] One type of thin film solar cell that has lately gained prominence is Dye-Sensitised Solar Cell (DSSC).[6]

A dye-absorbed nanocrystalline porous semiconductor electrode, a counter electrode, and an electrolyte containing iodide and triiodide ions make up a DSSC.[7] The dye, which acts as a photosensitiser in DSSCs, is a key component for receiving sunlight and converting it into electric energy.[8] As sensitisers, a variety of metal complexes and organic dyes have been explored.[9] DSSCs sensitised by Ruthenium-containing compounds absorbed on nanocrystalline TiO_2 had the highest efficiency, reaching 11–12[8] %.

However, considering Ruthenium is a noble metal and is also known to be highly toxic, its use as a sensitiser in DSSC raises safety concerns.[10] Although alternative synthetically manufactured dyes have been attempted to

Received : 19 February 2022, Revised : 30 January 2023
Accepted : 16 February 2023, Online published : 07 June 2023

replace Ru, the chemical synthesis procedure is arduous and time-consuming. Furthermore, synthetic dyes must be tested for toxicity before being used in a DSSC. Organic dyes derived from natural sources, on the other hand, are a more cost-effective solution that can be utilised without risk.[11]

Many organic dyes have been explored for their application in DSSC of which carotenoids and anthocyanins from different parts of plants such as fruits, flowers, and leaves have shown promising potential to be used as dye sensitisers.[12] However, using plants as a source of organic dyes has certain limitations. Dyes derived from plants are relatively costly due to several drawbacks such as instability (to light, heat, or an acidic pH), limited range, non-availability throughout the year, and complicated extraction techniques.[13]

Furthermore, while plants are the world's primary source of food and feed, microbes can be a great alternative for the commercial exploitation of pigments in the solar cell sector. Microbial dyes provide a number of advantages, including lower production costs, possibly quicker extraction, higher yields, no raw material shortages, and no seasonal dependance[14], making them a viable DSSC alternative. *Rhodococcus kroppenstedtiiis* an orange-red pigmented, gram-positive actinobacterium.[15] Carotenoids are produced in the membrane of this non-photosynthetic bacterium to protect the cell from oxidative damage.[16] *R. kroppenstedtii* can be grown at a large scale and the biomass can be used to extract carotenoids for a variety of uses.The ability of an ethanolic pigment extract from *Rhodococcus kroppenstedtii* as a photosensitiser in a DSSC was investigated in this study.

2. METHODOLOGY

2.1 Chemicals and Reagents

Tryptic Soy Broth, Agar-Agar, Glycine, Citric acid, Tris, and TiO_2 were purchased from Hi-media laboratories Pvt. Ltd. Ethanol, Glacial acetic acid, HCl, Na_2HPO_4 Iodine crystals, KI, NaOH were purchased from Sisco Research Laboratories (SRL) Pvt. Ltd. and Shilpent Tin oxide FTO coated conductive glass (25x25x2.2mm, Resistivity 15 *ohms/sq*) were purchased from Shilpa Enterprises, Nagpur, India, NUTEN Digital Multimeter was purchased from Jainone Hub, Delhi, India.

2.2 Microorganism

An orange-red pigmented action bacterium *Rhodococcus kroppenstedtii* (Accession No. MH715196) was isolated from Rajapur hot springs of Ratnagiri district, Maharashtra, India. The culture was maintained on Tryptic Soy Agar at 4 °C and subcultured regularly.

2.3 Extraction of Carotenoid

Extraction of carotenoid was done by solvent extraction method using ethanol as a solvent.[17] Briefly, the culture was grown in tryptic soy broth at 37 °C for 96 h at 110 *rpm*. The biomass was collected by centrifugation at 4500 *rpm* for 10min. The cell pellet was washed twice with D/W and carotenoid was extracted using ethanol. The UV-Vis absorption spectrum of crude ethanolic pigment extract displayed absorbance maxima of 475 *nm*, indicating the presence of carotenoids.

2.4 Stability Studies on the Carotenoid Extract

Instability is one of the major concerns of natural pigments due to which their usage as dye sensitisers in DSSC becomes difficult.[18] Thus, checking the pH, temperature, and photostability of the crude carotenoid extract was attempted to ascertain its potential application in DSSC.

For carrying out the stability studies[19], the carotenoid extract was concentrated using a rotary evaporator and dried at 37 °C. The dried extract was reconstituted in ethanol to obtain an absorbance of ~1.0 at 475 *nm*. For the temperature stability studies, the extract was dispensed in glass vials and exposed to different temperatures (0, 4, 10, 25, 32, 40, 60 & 80 °C) and absorbance was monitored at 475 *nm* up to 120 h. To determine the pH stability, the extract was mixed in a ratio of 1:1, with buffers (Table 1) ranging from pH 3-10.

Table 1. Solvent proportions ($^v/v$) used in buffer solutions

S. No.	pH	A (mL)	B (mL)	C (mL)	D (mL)	E (mL)	F (mL)	Final volume (mL)
1	3	39.8	10.2	--	--	--	--	100
2	4	29.4	20.6	--	--	--	--	100
3	5	24.3	25.7	--	--	--	--	100
4	6	16.9	33.1	--	--	--	--	100
5	7	6.5	43.6	--	--	--	--	100
6	8	--	--	50	21.9	--	--	200
7	9	--	--	50	5.0	--	--	200
8	10	--	--	--	--	50	32	200

A-0.1M Citric acid, B- 0.2M Na_2HPO_4, C- 0.1M Tris, D- 0.1M HCl, E- 0.1M Glycine, F- 0.1M NaOH

Absorbance was monitored at 475 *nm* for up to 15 days. Photostability studies were carried out by exposing the extract to different light conditions (dark, white light, and sunlight) and the absorbance was monitored at 475 *nm* for up to 15 days. All the experiments were carried out in triplicates.

2.5 Fabrication and Testing of Dye-Sensitised Solar Cell (DSSC) Sensitised Using the Carotenoid Extract from *R. Kroppenstedtii*

Fabrication of DSSC: Fabrication of a dye-sensitised solar cell assembly represented in Fig. 1, requires preparation of photo-anode and cathode.[11] The anode comprises of dye and TiO_2 molecules whereas the cathode consists of graphite coated on a conductive glass surface.

Preparation of anode: 20 *mL* of glacial acetic acid was slowly added to 12 g titanium dioxide (TiO_2) powder and mixed vigorously using a mortar and pestle. The FTO glass plate (area 2.25 cm^2) was coated evenly with the slurry of TiO_2 and then heated at 450 °C for 30 min. The annealed surface was then soaked in carotenoid extract for 30 min and allowed to dry overnight. The carotenoid extract at different concentrations (12.5-100 *mg/mL*) was used for sensitisation of TiO_2 in a DSSC assembly.

Preparation of cathode: A fresh conductive glass plate was used for preparing the cathode surface. The FTO glass plate was coated with a carbon film (using a graphite pencil) making sure that the 2.25 cm^2 area was uniformly coated. Annealing was performed by heating at 450 °C for 10 min. The cathode part of DSSC was ready to assemble.

Assembly and Testing of DSSC:The electrodes were offset by placing the carbon-coated side of the cathode on the dye-coated side of the anode. The alligator wires connecting to a multimeter were clipped into each of the electrodes. The 0.1 N iodine solution prepared in 3 % KI was slowly inserted along an offset edge between the two electrodes. This allowed uniform distribution of electrolytes among the graphite coating and the layer of TiO_2- carotenoid complex. The assembled DSSC was connected to a multimeter using alligator clips and wires. The DSSC assembly was then illuminated using an artificial light source (100 *W* incandescent bulb) to measure the current (I) and voltage (V) response.The power output (P) of the cell was calculated by measuring the current and voltage response against varying concentrations of the carotenoid extract fabricated on the DSSC using the following formula[21];

$$P = I \times V$$

where, P = power output (*mW*), I = current (*mA*) and V = voltage (*mV*)

Further to check its stability, the power output of DSSC was monitored for 8 days.

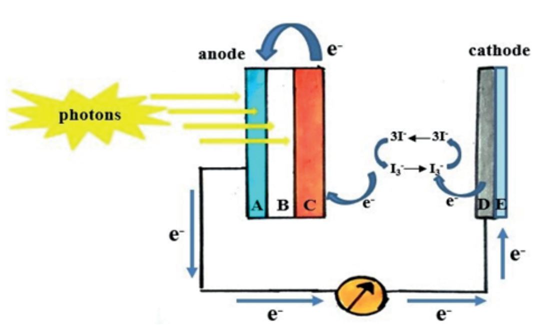

Figure 1. Assembly of DSSC: A and E= Conductive glass, B= TiO_2 layer, C= carotenoid extract from *Rhodococcus kroppenstedtii*, D=Graphite layer, I- and I³=Electrolyte.

3. RESULTS AND DISCUSSION

3.1 Stability Studies on the Carotenoid Extract

Carotenoids, like other natural colorants, suffer from instability, which is impacted by their nature (carotene or xanthophyll, E- or Z-configuration, esterified or unesterified).[22] The severity of variables such as pH, temperature, oxygen, and so on, as well as the duration and exposure to light, all contribute to their degradation.[23] Their stability in various environmental conditions must be tested before they can be used as dye sensitisers. Hence, the stability of carotenoid extract in various environmental conditions such as pH, temperature, and the light was assessed before its consideration as a photosensitiser.

The temperature stability studies for the period of 120 h showed that at temperatures 0-40 ºC the extract exhibited 90 % stability. Above 40 ºC, the extract was found to be stable up to 24 h, beyond which a downward trend in stability was observed (Fig. 2). The pH stability studies (Fig. 3) suggested that the carotenoid extract was stable in pH 4-6 till the end of the study period (15 days). Further, photostability studies conducted for 15 days (Fig. 4) showed that the extract was stable in white light. However, when exposed to sunlight, a slight decline in stability was observed. Overall, the carotenoid extract exhibited good stability and hence an attempt was made to assess its suitability as a photosensitiser.

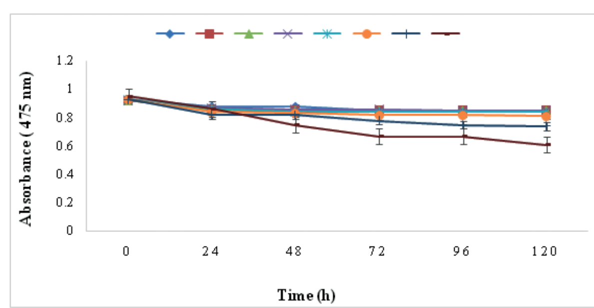

Figure 2. Temperature stability profile of carotenoid extract from *Rhodococcus kroppenstedtii*.

3.2 Use of Microbial Carotenoid as Dye Sensitiser in DSSC

In the present study, increasing concentrations (12.5–100 *mg/mL*) of the carotenoid extract from *R. kroppenstedtii* were used for the sensitisation of TiO_2 in a DSSC assembly. The extract showed a linear rise in power output (078±0.0001 *mW* - 20.75±0.0003 *mW*) with increasing concentration (Fig. 5). Also, the DSSC was monitored for stability in power output for 8 days. The power output remained stable at the end of the study period (8 days) as depicted in Fig. 6.

Thus, this study demonstrates the potential of microbial carotenoids as a stable and economical photosensitiser in a Dye-Sensitised Solar Cell (DSSC). The current work was a preliminary investigation on the suitability of carotenoids derived from *R. kroppenstedtii* as a photosensitiser. Future studies are required to evaluate the efficiency of solar cells and their comparison with other plant-based sensitisers.

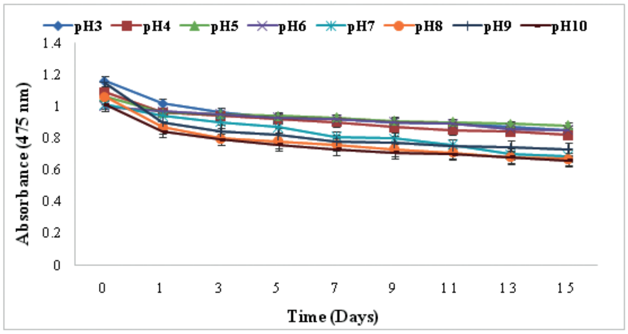

Figure 3. pH stability profile of carotenoid extract from rhodococcus kroppenstedtii.

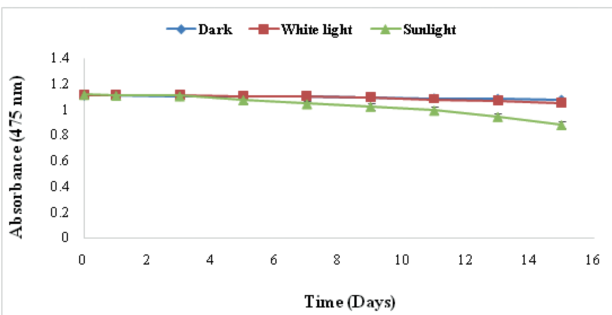

Figure 4. Light stability profile of carotenoid extract from Rhodococcus kroppenstedtii.

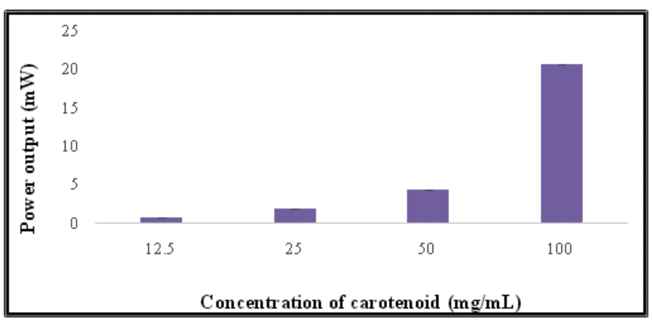

Figure 5. Effect of concentration of the carotenoid extract on the power output of DSSC.

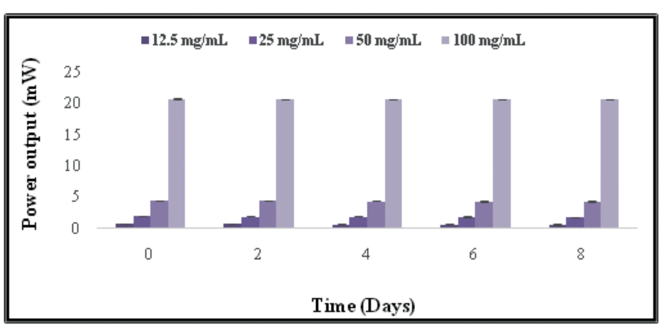

Figure 6. The power output of DSSC as a function of time.

4. CONCLUSION

The present work was the first attempt of using carotenoid from a non-photosynthetic actinobacteria *Rhodococcus kroppenstedtii* as a photosensitiser in a DSSC. The biomass from *R. kroppenstedtii* was used for the extraction of carotenoids using the solvent extraction method. The stability studies indicated that the carotenoid extract can withstand different temperatures, pH, and light conditions and thus can be effectively employed as a photosensitiser in a DSSC. The increasing concentrations of the carotenoid extract fabricated on the DSSC assembly led to a linear and stable increase in power output.Thus demonstrating that microbe-based photosensitisers have strong potential in the field of renewable energy to overcome the sustainability challenges faced by synthetic dyes.

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