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Performance of Papaya Leaves Chlorophyll-Based DSSC with Deoxycholic Acid

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Abstract. *Natural chlorophyll dyes offer an environmentally friendly alternative to synthetic sensitizers in DSSCs, but their relatively low stability and aggregation on TiO_2 surfaces limit photovoltaic performance. This study investigated the optimum chlorophyll extraction conditions from papaya leaves (Carica papaya L.) using Microwave-Assisted Extraction (MAE) and the effect of Deoxycholic Acid (DCA) as a co-adsorbent on Dye-Sensitized Solar Cell (DSSC) performance. Chlorophyll was extracted using acetone and ethanol for 1–4 minutes, while DSSCs were fabricated with DCA concentrations of 0–5 mM. The highest chlorophyll yield was obtained using acetone for 2 minutes, producing total chlorophyll, chlorophyll a, and chlorophyll b contents of 12.024%, 7.342%, and 4.681%, respectively. DSSC performance improved with DCA addition up to 4 mM, achieving a Voc of 1.310 V, Isc of 1.22 × 10^{-4} A, output power of 1.35 × 10^{-4} W, and efficiency of 1.533%, representing a 195.4% increase compared with the control. A higher DCA concentration (5 mM) reduced efficiency due to competition for adsorption sites on the TiO_2 surface. The optimum DSSC performance was achieved using chlorophyll extracted with acetone for 2 minutes and 4 mM DCA as a co-adsorbent.*

Keywords: *papaya leaves, chlorophyll, microwave-assisted extraction, dye-sensitized solar cell, deoxycholic acid.*

Type of the Paper: Regular Article

1. Introduction

The increasing global demand for sustainable and environmentally friendly energy technologies has accelerated the development of third-generation photovoltaic systems. Among these technologies, Dye-Sensitized Solar Cells (DSSCs) have attracted considerable attention due to their low fabrication cost, simple manufacturing process, transparency, and ability to operate under diffuse light conditions. Unlike conventional silicon-based solar cells, DSSCs utilize dye molecules adsorbed onto semiconductor surfaces to harvest solar energy and convert it into electricity. DSSC performance is strongly influenced by the optical and electronic properties of the sensitizer, making the exploration of natural dyes an important research direction for developing eco-friendly photovoltaic devices. Recent advances in DSSC technology have highlighted the importance of optimizing dye adsorption and charge-transfer processes to enhance photovoltaic efficiency [1,2].

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Natural pigments derived from plant materials have emerged as promising alternatives to expensive synthetic ruthenium-based dyes because of their abundance, biodegradability, and low toxicity. Among various natural pigments, including anthocyanin, betalains, carotenoids, cyanin, chlorophyll, and tannin, chlorophyll has demonstrated considerable potential as a DSSC sensitizer due to its broad absorption in the visible light region and intrinsic role in natural photosynthesis compared to anthocyanin and betalains, which degrade very quickly under solar radiation [3]. Papaya leaves (*Carica papaya* L.) represent an attractive source of chlorophyll because they are widely available agricultural biomass with high chlorophyll content and minimal economic value. Previous studies have shown that chlorophyll extracted from papaya leaves exhibits favorable optical characteristics for solar energy conversion applications, suggesting its potential as a low-cost sensitizer in DSSC systems [4,5].

The extraction method plays a crucial role in determining the concentration, purity, and stability of chlorophyll pigments. Conventional extraction techniques often require long processing times and large solvent volumes, which may lead to pigment degradation and reduced extraction efficiency. Microwave-Assisted Extraction (MAE) has emerged as an efficient alternative because microwave energy enhances cell wall disruption and accelerates mass transfer, resulting in faster extraction and improved recovery of bioactive compounds. Recent studies have demonstrated that MAE significantly improves chlorophyll extraction yield while reducing extraction time, energy consumption, and solvent requirements compared with conventional extraction methods [6,7]. Furthermore, extraction parameters such as solvent type and extraction duration substantially affect chlorophyll yield, pigment stability, and antioxidant properties, which ultimately influence the optical characteristics and photovoltaic performance of DSSCs [8,9]. Therefore, optimization of extraction conditions is essential for obtaining high-quality chlorophyll sensitizers suitable for photovoltaic applications.

In addition to dye quality, the adsorption behavior of sensitizer molecules on the TiO_2 surface is a critical factor governing DSSC performance. Chlorophyll molecules tend to aggregate on semiconductor surfaces, reducing effective electron injection and increasing charge recombination. To overcome this limitation, co-adsorbents are commonly introduced to improve dye dispersion and surface coverage. Chenodeoxycholic acid (CDCA) is widely recognized as a benchmark co-adsorbent in DSSCs because it suppresses dye aggregation and enhances photovoltaic efficiency [2,10]. Recent theoretical and experimental studies have demonstrated that bile-acid-based co-adsorbents significantly improve charge-transfer characteristics, facilitate electron injection, and reduce recombination losses by regulating dye packing on TiO_2 surfaces [1,11]. Since deoxycholic acid (DCA) possesses a molecular structure similar to that of CDCA, it is expected to exhibit comparable anti-aggregation behavior while providing an alternative co-

adsorbent for natural dye-based DSSCs. The selection of DCA is particularly relevant for natural-dye-based DSSCs because natural pigments can exhibit extensive intermolecular interactions and aggregation when adsorbed onto TiO_2, potentially limiting effective electron injection. Previous experimental studies showed that DCA reduced dye aggregation while increasing photocurrent density, and electrochemical measurements indicate that DCA co-adsorption could extend electron lifetime and improve the open-circuit voltage [12,13].

Recent investigations on DSSCs employing chlorophyll and natural dye systems have confirmed that co-adsorbent incorporation can substantially improve photovoltaic performance by enhancing electron injection efficiency and minimizing intermolecular aggregation. Tutar et al. [11] reported that incorporationing co-adsorbents into chlorophyll-based DSSCs improved dye organization at the photoanode interface, resulting in enhanced charge transport and reduced recombination. Similarly, computational studies by Saha and Ganguly revealed that co-adsorbent molecules improve photovoltaic efficiency through optimized dye adsorption geometry and more favorable electronic interactions with TiO_2. These findings [1] indicate that the synergistic optimization of dye extraction conditions and co-adsorbent concentration is crucial for achieving higher DSSC efficiency.

Therefore, this study aims to investigate the efficiency of DSSCs based on chlorophyll extracted from papaya leaves using Microwave-Assisted Extraction (MAE) and deoxycholic acid (DCA) as a co-adsorbent. The effects of three treatment variables: solvent type, extraction time, and DCA concentration were evaluated to determine their influence on chlorophyll characteristics and photovoltaic performance. The findings are expected to provide valuable insights into the development of sustainable natural dye sensitizers and contribute to the advancement of environmentally friendly DSSC technology.

2. Materials and Methods

The first stage in this study was the extraction of chlorophyll from papaya leaves. Papaya leaves were washed first, then drained and cut into pieces measuring 5 cm ± 0.5 cm, dried at 50ºC to a moisture content of 6% ± 0.5%, and powdered and sieved through an 80-mesh sieve (177 microns). In the chlorophyll extraction process, papaya leaves powder was mixed with $NaHCO_3$ as a stabilizer at a concentration of up to 3%, followed by the addition of acetone or ethanol at a material-to-solvent ratio of 1:10. Chlorophyll was extracted using the Microwave-Assisted Extraction method with the specified extraction time (1, 2, 3 and 4 minutes). Subsequently, the filtrate was filtered using Whatman No. 1 filter paper and evaporated in a rotary vacuum evaporator at a pressure of 0.18 atm and a temperature of 50 °C, thereby yielding the optimal extract based on the best solvent. Chenodeoxycholic acid was then added as a co-adsorbent (at concentrations

of 0, 1, 2, 3, 4, and 5 mM) to the papaya leaf extract with the highest chlorophyll content for the subsequent stage.

The second stage involves immersion of FTO-TiO_2 in papaya leaf extract, following the study by Sari et al. [14], who found that fluorine-doped tin oxide (FTO) glass coated with TiO_2 exhibited the best performance when immersed in chlorophyll for 60 hours. The third stage involves the creation of gel electrolytes. The gel electrolyte used in this study is based on research conducted by Hartati et al. [15], to make an electrolyte solution, combining 3 grams of Potassium Iodide (KI) and 3 ml of 10% liquid iodine solution, then stirred for 30 minutes. Meanwhile, the polymer material for the gel electrolyte consisted of 2.5 g of polyethylene glycol (PEG) 1000 dissolved in 5 ml of acetonitrile. The electrolyte solution and polymer material were mixed using a stirrer for 60 minutes at 85°C. Then, the previously prepared liquid electrolyte was added to the polymer solution for 60 minutes at 85°C until it became a gel electrolyte.

The fourth stage was the assembly of the DSSC prototype. During assembly, an anode bonded with chlorophyll was sandwiched between a platinum-coated cathode. The assembled layers were then coated with a gel electrolyte solution.

The experiment was arranged in a Completely Randomized Design (CRD). The independent variable was the concentration of Deoxycholic Acid (DCA) added to the papaya leaves chlorophyll extract, with six treatment levels: 0 mM (control), 1 mM, 2 mM, 3 mM, 4 mM, and 5 mM. All DSSC prototypes were fabricated and measured in triplicate to ensure reproducibility and statistical validity.

The observed variables were the chlorophyll content, the short-circuit current value (Isc), open-circuit voltage value (Voc), fill factor value (FF), and efficiency value (η) of the assembled DSSC prototype. The statistical significance of DCA concentration on DSSC performance parameters was evaluated using One-Way Analysis of Variance (ANOVA). Statistically significant differences ($p \leq 0.05$) among the treatment means were further analyzed using Tukey's Honestly Significant Difference (HSD) post-hoc test.

3. Result and Discussion

2.1. Papaya Leaves Powder

During the raw material preparation stage, the average yield of papaya leaves powder was 9.99%. Meanwhile, the average moisture content of papaya leaf powder was 5.854%. The SEM image of the chlorophyll extracted from papaya leaf powder is shown in Fig. 1.

2.2. Chlorophyll Content

The results shown in Table 1 indicate that the type of solvent and extraction time using Microwave-Assisted Extraction (MAE) affected the levels of total chlorophyll, chlorophyll a, and

chlorophyll b. In general, acetone produced higher chlorophyll levels than ethanol at all observed extraction times. This indicates that acetone has a better ability to dissolve chlorophyll pigments because its polarity matches the characteristics of chlorophyll molecules and enables more effective penetration of plant cell membranes. Various studies have reported that acetone is one of the most efficient solvents for chlorophyll extraction compared to ethanol, especially for quantitative analysis of chlorophyll a and b [16–18].

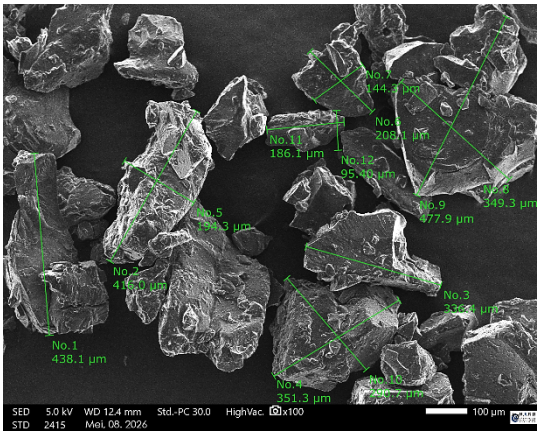


Fig.1 SEM image of Papaya Leaves Powder.

Table 1. Chlorophyll Content of Papaya Leaves.

Parameter	Solvents	Extraction Time (minutes)			
		1	2	3	4
Chlorophyll total (%)	Acetone	10.600±0.301	12.024±0.121	10.785±0.366	10.096±0.040
	Ethanol	10.086±0.094	10.160±0.136	9.799±0.059	8.889±0.104
Chlorophyll a (%)	Acetone	6.871±0.100	7.342±0.104	7.133±0.021	6.372±0.044
	Ethanol	6.416±0.089	6.807±0.149	6.177±0.052	5.394±0.052
Chlorophyll b (%)	Acetone	3.729±0.223	4.681±0.039	3.652±0.377	3.724±0.021
	Ethanol	3.670±0.015	3.353±0.099	3.622±0.043	3.494±0.056

2.3. Chlorophyll Total

Fig. 2 shows chlorophyll extracts obtained from papaya leaves (Carica papaya L.) using acetone as the extraction solvent at a solvent-to-substrate ratio of 10:1. The extracts were contained in sealed test tubes and exhibited varying shades of green, indicating differences in chlorophyll concentration resulting from the extraction treatments. The highest total chlorophyll content was obtained with acetone at an extraction time of 2 minutes (12.024 ± 0.121%), while the lowest content was obtained with ethanol at an extraction time of 4 minutes (8.889 ± 0.104%). In both solvents, an increase in total chlorophyll content was observed from the first to the second minute, indicating that extending the extraction time to 2 minutes enhanced pigment release from the leave cell matrix. This condition indicates that microwave energy applied at the beginning of the process can accelerate cell wall damage and increase mass transfer, resulting in greater pigment extraction. With acetone, the content dropped to 10.785% at 3 minutes and 10.096% at 4 minutes, while with ethanol, the decrease was more pronounced, reaching 8.889% at 4 minutes. This decrease is likely

caused by thermal degradation of chlorophyll due to longer microwave exposure, resulting in the conversion of some chlorophyll into derivative compounds such as phesophytin. A similar phenomenon has been reported in various MAE studies, where excessively long extraction times cause pigment damage due to increased local temperatures during the extraction process [9,16,19].

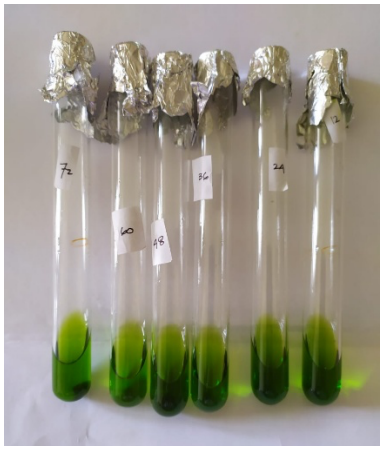


Fig.2 Papaya Leaves Chlorophyll Extract using Acetone at 10:1.

2.4. Chlorophyll α

Chlorophyll a is the main component of total chlorophyll; therefore, the observed trends were relatively similar. The highest chlorophyll a levels were obtained with acetone treatment for 2 minutes (7.342 ± 0.104%), while the lowest levels were obtained with ethanol for 4 minutes (5.394±0.052%). Acetone produced higher chlorophyll a levels than ethanol at all extraction times. This indicates that acetone is more effective in dissolving chlorophyll a, which is relatively hydrophobic due to the presence of phytol chains in its structure. The increase in levels up to the 2nd minute indicates that microwave energy reached optimum conditions for pigment release from the sample tissue. Thereafter, chlorophyll a levels decreases at the 3rd and 4th minutes, indicating degradation due to excessive heating. Chlorophyll a is susceptible to loss of magnesium ions from the porphyrin ring, forming pheophytin when exposed to heat for a long time [9,16,20]. The predominance of chlorophyll a over chlorophyll b across all treatments aligns with the natural composition of green leaves, in which chlorophyll a is the primary photosynthetic pigment and is generally present in higher quantities than chlorophyll b [16,21].

2.5. Chlorophyll b

Chlorophyll b levels showed a slightly different pattern compared to chlorophyll a. In the acetone treatment, chlorophyll b levels increased from 3.729% to 4.681% at 2 minutes, then decreased at 3 minutes and remained relatively stable at 4 minutes. In the ethanol treatment, chlorophyll b levels were generally lower and fluctuated in the range of 3.353–3.670%. The high chlorophyll b levels in the 2-minute acetone treatment indicate that this condition was optimal for extracting accessory pigments without causing significant degradation. The decrease after the optimum time indicates that chlorophyll b also experiences damage due to excessive heat

exposure, although its stability may differ from that of chlorophyll a due to differences in the functional groups in the porphyrin ring [16,20].

2.6. The Effect of Interaction between Solvent Type and Extraction Time

Fig. 3 shows assembled Dye-Sensitized Solar Cell (DSSC) devices fabricated using papaya leaf chlorophyll extract as the natural sensitizer. Each DSSC consists of two fluorine-doped tin oxide (FTO) glass substrates sandwiched together, with the chlorophyll dye adsorbed onto the TiO_2 photoanode and a gel electrolyte placed between the electrodes. Binder clips were used to hold the FTO glass layers firmly in place during characterization. The dark green coloration visible in the active area indicates the successful adsorption of chlorophyll molecules onto the TiO_2 surface. In this study, a co-adsorbent (deoxycholic acid, DCA), was added to improve dye distribution and reduce chlorophyll aggregation on the photoanode, thereby enhancing electron injection and overall DSSC performance. The assembled cells were subsequently evaluated for their photovoltaic characteristics, including open-circuit voltage, short-circuit current, and conversion efficiency. Overall, the combination of acetone and a 2-minute extraction time was the best treatment for producing the highest levels of total chlorophyll, chlorophyll a, and chlorophyll b. These results indicate that the success of chlorophyll extraction with MAE is determined by the solvent's ability to dissolve pigments and the duration of microwave exposure. Too short an extraction time may not optimally extract all pigments, while excessive extraction time can cause chlorophyll degradation due to increased temperature. Therefore, optimizing both factors is crucial for obtaining high-quality and high-concentration chlorophyll extracts. These findings align with research by Georgiopoulou et al. [9], who reported that MAE significantly increases pigment extraction efficiency at an optimal extraction time, but increasing the extraction duration after the optimum point actually decreases the extract quality due to the degradation of heat-sensitive compounds [19]. Effect of DCA concentration on DSSC efficiency is shown in Fig. 4.

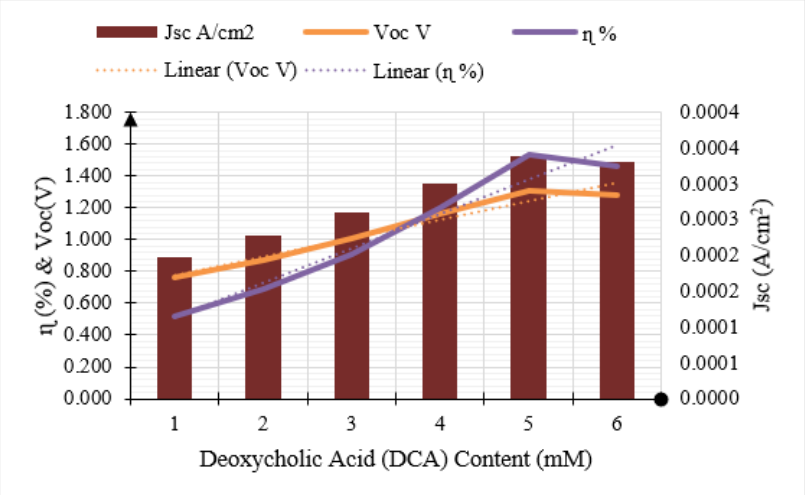


Fig. 3. FTO glass that has been sandwiched with papaya leaves chlorophyll extract and gel electrolyte with the addition of a co-adsorbent.

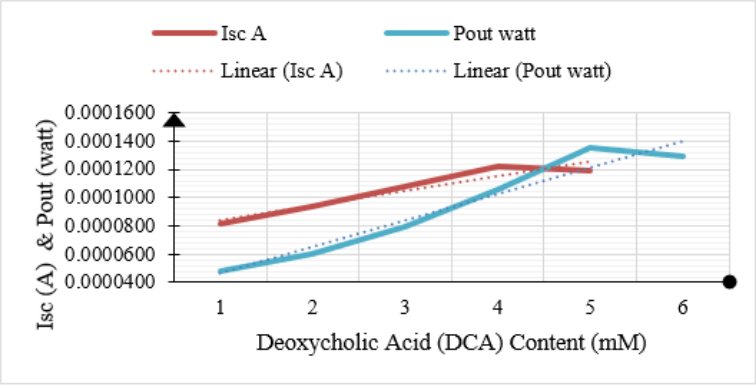


Fig.4. Effect of DCA concentration on DSSC efficiency, Open-Circuit Voltage and Short-Circuit Current Density.

2.6.1. Effect of DCA on DSSC Performance

The plot of efficiency (η) versus DCA concentration (0–5 mM) reveals a positive parabolic curve (a volcano-shaped trend), as shown in Fig 4. Efficiency increases gradually from 0.519% to 1.533% at 4 mM, then declines to 1.460% at 5 mM. Similar trends are observed for Voc, Isc, Jsc, and Pout. This pattern indicates that DCA acts as a co-adsorbent, enhancing the photovoltaic process up to an optimal point before competitive adsorption effects occur at excessively high concentrations. Similar phenomena have been widely reported in DSSCs employing bile acids such as deoxycholic acid (DCA) or chenodeoxycholic acid (CDCA) [12,13].

2.6.2. The Relationship Between DCA and Open-Circuit Voltage (Voc)

The plot of Voc versus DCA concentration in Fig. 4 shows a nearly linear increase from 0.762 V to 1.310 V at 4 mM. This 71.9% increase indicates a reduction in the electron recombination rate at the TiO_2/electrolyte interface. In a DSSC, Voc is determined by the difference between the electron Fermi level in the TiO_2 and the redox potential of the electrolyte. When recombination decreases, the TiO_2 Fermi level shifts toward higher energy, increasing Voc [22,23].

2.6.3. The Relationship Between DCA and Short-Circuit Current Density (Jsc)

As shown in Fig. 4, the Jsc value increased from 0.0002 to 0.0003 A/cm². Although the numerical change appears small due to data rounding, the graph trend indicates a consistent increase up to 4 mM. In DSSCs, Jsc is influenced by three main factors: the amount of light absorbed, electron injection efficiency, and electron collection efficiency. DCA contributes to these three factors by modulating dye adsorption [24,25].

2.6.4. Short-Circuit Current (Isc) and Output Power (Pout) Trend

The Isc curve in Fig. 5 shows an increase from 7.11×10^{-5} A to 1.22×10^{-4} A at 4 mM DCA. This approximately 71.6% increase indicates that a greater number of photons are successfully converted into electrons that can be collected at the electrode. In the graph, the Isc pattern is nearly

identical to the efficiency pattern, demonstrating that the increase in current is the dominant factor driving the rise in PCE.



Fig.5. Effect of DCA concentration on Short-Circuit Current and Output Power.

The output power (Pout) graph shows a nearly threefold increase—from 4.58×10^{-5} W to 1.35×10^{-4} W—at 4 mM DCA. This curve is strongly correlated with the efficiency graph, as the PCE is calculated based on the ratio of output power to incident light power. The increase in Pout indicates that more electrons are generated and transported more effectively to the electrode.

2.7. Efficiency of Dye-Sensitized Solar Cell

The results of the DSSC efficiency test shown in Table 2 indicate that the addition of Deoxycholic Acid (DCA) as a co-adsorbent affected the photovoltaic performance of DSSC using papaya leaves chlorophyll extract as a dye sensitizer. In this study, the chlorophyll extract was first stabilized using 3% $NaHCO_3$, which functions to maintain Mg^{2+} ions in the chlorophyll porphyrin structure, thereby inhibiting the formation of pheophytin during the extraction and adsorption process on the TiO_2 surface. Better chlorophyll stability increases the light absorption capacity and maintains the electron injection process into the TiO_2 conduction band. This finding aligns with various studies reporting that controlling pH conditions and chlorophyll stability are important factors in improving the performance of natural dye-based DSSCs [26,27].

Table 2. Output Power and Efficiency of Dye Sensitized Solar Cell.

DCA Content	Voc	Vmpp	Isc	Impp	Jsc	Jmpp	Pout	FF	Pmax	η
mM	V	V	A	A	A/cm^2	A/cm^2	watt		watt	%
0	0.762	0.759	7.11×10^{-5}	6.03×10^{-5}	0.0002	0.0002	4.58×10^{-5}	0.845	0.0001	0.519
1	0.876	0.873	8.18×10^{-5}	6.93×10^{-5}	0.0002	0.0002	6.05×10^{-5}	0.845	0.0002	0.686
2	1.008	1.004	9.40×10^{-5}	7.98×10^{-5}	0.0003	0.0002	8.00×10^{-5}	0.845	0.0002	0.908
3	1.159	1.154	1.08×10^{-4}	9.17×10^{-5}	0.0003	0.0003	1.06×10^{-4}	0.845	0.0003	1.200
4	1.310	1.304	1.22×10^{-4}	1.04×10^{-4}	0.0003	0.0003	1.35×10^{-4}	0.845	0.0004	1.533
5	1.278	1.273	1.19×10^{-4}	1.01×10^{-4}	0.0003	0.0003	1.29×10^{-4}	0.845	0.0004	1.460

The fill factor (FF) values of the DSSC across various DCA concentrations demonstrated remarkable stability, ranging from 0.8450 to 0.8454. In practical terms, all values remained identical (0.845) when rounded to three decimal places, indicating no significant difference. Statistical analysis confirmed that variations in DCA concentration did not significantly affect the FF. Nevertheless, a very slight increase in FF was observed as the DCA concentration rose from 0 mM to 4 mM, followed by a minor decrease at 5 mM. This trend suggests that the addition of DCA plays a more significant role in enhancing charge transfer processes and solar cell efficiency than in influencing the internal resistance or recombination mechanisms that determine the FF value. The stability of the FF indicates that the quality of the DSSC current-voltage curve remained relatively unchanged across treatments, given that the fill factor in DSSCs is primarily influenced by series resistance, shunt resistance, and charge loss due to recombination [28,29].

The addition of DCA to the TiO_2 photoanode surface functions as a co-adsorbent that reduces the aggregation of chlorophyll molecules. Without a co-adsorbent, chlorophyll molecules tend to form aggregates through intermolecular interactions, resulting in the loss of some excitation energy through recombination and quenching. DCA acts as a "spacer" that separates chlorophyll molecules on the TiO_2 surface, resulting in a more homogeneous dye distribution and a more efficient electron injection. Consequently, increasing the DCA concentration to the optimal level is generally followed by an increase in short-circuit current (Jsc), fill factor (FF), and power conversion efficiency (PCE) [11].

Based on the data in Table 2, the addition of DCA has a very significant effect on all DSSC photovoltaic parameters: Voc, Isc, Jsc, Pmax, and power conversion efficiency (η). In general, increasing the DCA concentration from 0 to 4 mM gradually increases DSSC performance, while a slight decrease occurred at 5mM. This indicates that the optimum DCA concentration in the DSSC system based on papaya leaves chlorophyll stabilized with 3% $NaHCO_3$ is at 4 mM.

The Voc value increased from 0.762 V in the control (0 mM) to 1.310 V at 4 mM DCA, representing an increase of approximately 71.9%. This increase in Voc indicates that DCA can reduce the rate of electron recombination between the TiO_2 conduction band and the electrolyte. DCA molecules fill the spaces between the chlorophyll molecules adsorbed on the TiO_2 surface, forming a denser layer and reducing direct contact of the electrolyte and semiconductor surface. As a result, electrons injected from chlorophyll to TiO_2 have a longer lifetime, thus increasing the output voltage. This mechanism is the main function of co-adsorbents in DSSCs [30,31].

The Isc value increased from 7.11×10^{-5} A in the control to 1.22×10^{-4} A in the 4 mM DCA treatment, representing an increase of approximately 71.6%. This increase indicates that more electrons were successfully generated and transferred to the electrode. DCA acts as an anti-aggregation agent that prevents the accumulation of chlorophyll molecules on the TiO_2 surface.

Without a co-adsorbent, chlorophyll molecules tend to aggregate, causing excitation quenching and reducing electron injection efficiency. In the presence of DCA, chlorophyll molecules are distributed more evenly, resulting in more effective light absorption and electron transfer[11,30].

The maximum output power (Pout) increased from 4.58×10^{-5} W in the control to 1.35×10^{-4} W in the 4 mM treatment. This increase in power aligns with the increase in Voc and Isc that occurred simultaneously. Meanwhile, the Fill Factor (FF) value remained constant at 0.845 in all treatments. This indicates that the addition of DCA does not significantly change the characteristics of the internal resistance of the cell, but instead improved the process of light absorption, electron injection, and reducing charge recombination. In other words, the increase in efficiency obtained mainly comes from the increase in voltage and current rather than changes in the quality of the electrical connections in the DSSC.

The efficiency of DSSC increased consistently from 0.519% in the control to 1.533% in the 4 mM DCA treatment, representing an increase in efficiency of 195.4%, or almost three times, compared to the control. This increase in efficiency indicates that the combination of 3% $NaHCO_3$ and 4 mM DCA improved two main factors that determine the performance of chlorophyll-based DSSC. $NaHCO_3$ functions to maintain the stability of the chlorophyll structure by preventing the formation of pheophytin under acidic conditions, thereby preserving the light-harvesting ability of chlorophyll pigments [32]. Studies have shown that chlorophyll stability is a critical factor affecting the photoelectrochemical performance of natural dye-based DSSCs because chlorophyll degradation reduces electron injection efficiency into the TiO_2 conduction band [33,34]. Meanwhile, DCA acts as a co-adsorbent that suppresses dye aggregation on the TiO_2 surface, improves dye distribution, reduces charge recombination, and facilitates more efficient electron transport. Recent studies have reported that bile-acid-based co-adsorbents significantly enhance dye packing and interfacial charge-transfer processes in DSSCs, leading to higher photovoltaic performance [2,35]. Similar findings were reported by Tutar et al. [11], who found that co-adsorbents effectively reduced chlorophyll aggregation and increased the power conversion efficiency of natural dye DSSCs [9,36]. Therefore, the synergistic effect of $NaHCO_3$ and 4 mM DCA promotes more effective light absorption, higher electron injection efficiency, and lower recombination losses, resulting in a substantial enhancement of DSSC efficiency [20,37].

At a concentration of 5 mM, the DSSC efficiency decreased from 1.533% to 1.460%, although it remained higher than other treatments. This decrease indicates that the DCA concentration has passed the optimum condition. At high concentrations, DCA begins to compete with chlorophyll molecules for adsorption sites on the TiO_2 surface. As a result, the number of chlorophyll molecules that can bind to the photoanode decreases, decreasing the light absorption

capacity. This adsorption competition has been widely reported in DSSC studies using bile acid-based co-adsorbents such as DCA and CDCA [30,31].

The addition of DCA was proven to improve the performance of papaya leaf chlorophyll-based DSSC stabilized with 3% $NaHCO_3$. Increasing the DCA concentration from 0 to 4 mM caused a gradual increase in Voc, Isc, Pout, and DSSC efficiency. The highest efficiency was obtained at a concentration of 4 mM DCA, with a value of 1.533%. This increase occurred because DCA functions as a co-adsorbent that reduces chlorophyll aggregation, increases electron injection into TiO_2, and suppresses charge recombination at the dye/TiO_2 interface. Previous studies have reported that co-adsorbents improve dye distribution on the TiO_2 surface and enhance charge-transfer processes, resulting in higher photovoltaic performance. Specifically, chenodeoxycholic-acid-type co-adsorbents have been shown to reduce intermolecular dye aggregation and improve electron transport efficiency in DSSCs. Furthermore, recent studies on natural dye-based DSSCs demonstrated that co-adsorbents effectively suppress the aggregation of chlorophyll and anthocyanin molecules, leading to significant increases in power conversion efficiency. Therefore, the enhancement observed in the present study indicates that 4 mM DCA provides sufficient surface coverage to optimize chlorophyll adsorption and electron injection. However, increasing the concentration to 5 mM decreased efficiency due to adsorption competition between DCA and chlorophyll molecules on the TiO_2 surface, reducing the amount of photoactive dye adsorbed. Thus, 4 mM DCA was the optimum concentration for papaya leaves chlorophyll-based DSSC in this study [38].

2.8. Electron Injection Efficiency and HOMO–LUMO Energy Level Alignment

In the DSSC mechanism, following photon absorption, an electron is excited from the dye's HOMO to its LUMO. The electron is then injected into the TiO_2 conduction band, provided the LUMO energy level lies above that band. DCA helps maintain a more favorable adsorption orientation, thereby enhancing the efficiency of electronic coupling between the dye and the TiO_2 [24,39,40].

The effectiveness of DSSCs depends on the positions of the dye's HOMO and LUMO energy levels relative to the TiO_2 conduction band and the electrolyte. The addition of DCA does not directly alter the energy levels of the chlorophyll molecules but reduces inter-dye interactions that could otherwise cause energy shifts due to excitonic coupling. Consequently, the energy alignment remains optimal for electron injection [24,40].

2.9. Correlation between Voc, Isc, and Efficiency

Scatter plot visualizations of efficiency versus Voc and efficiency versus Isc reveal a very strong positive correlation. This indicates that the increase in PCE results from the simultaneous

enhancement of voltage and current. Since the fill factor (FF) remained constant, changes in efficiency are almost entirely explained by changes in Voc and Isc.

2.10. Implications for Natural Dye-Based DSSCs

These results indicate that the natural dye chlorophyll has a primary limitation: molecular aggregation on the TiO_2 surface. The use of DCA successfully mitigated this limitation, resulting in an efficiency increase from 0.519% to 1.533%. This 195.4% improvement is highly significant for chlorophyll-based DSSCs and aligns with various reports on the use of co-adsorbents in both natural and organic DSSCs [11,24,41].

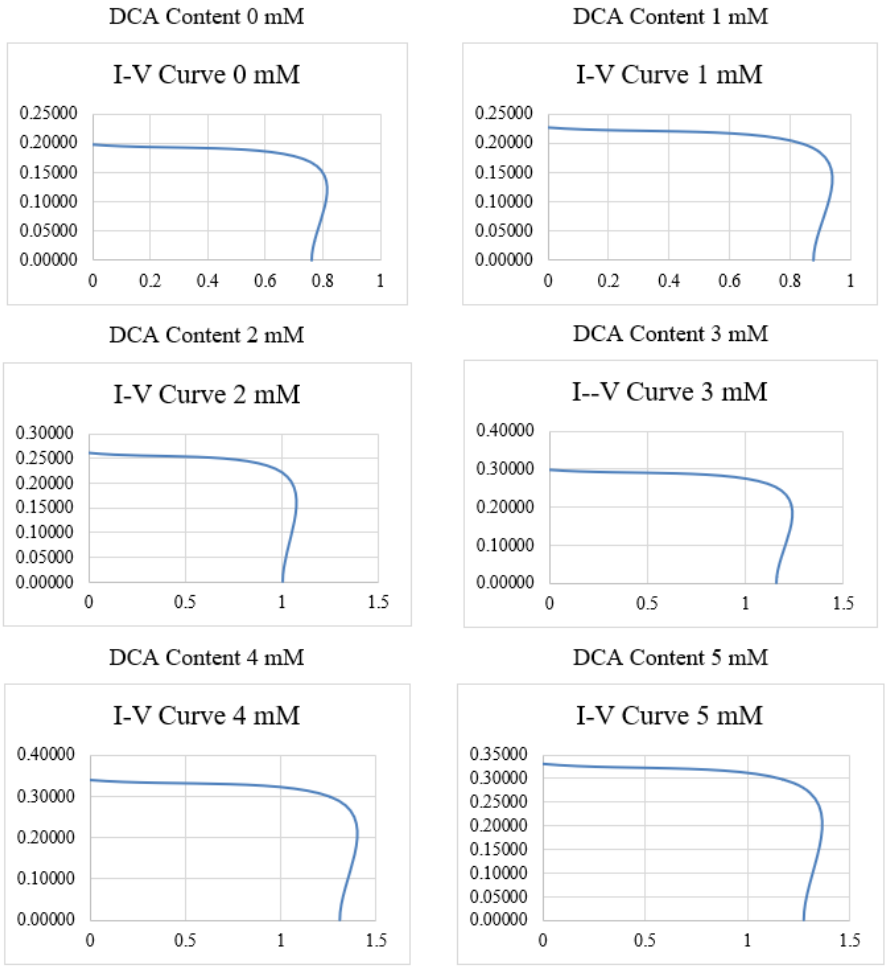


Fig. 6. I-V Curve of DSSC Output.

2.11. I-V Curve of DSSC Output

Based on the I–V curves of DSSCs utilizing papaya leaf chlorophyll as the dye sensitizer shown in Fig 6, increasing the DCA (deoxycholic acid) concentration from 0 to 4 mM caused the curve to shift to the right and upward, indicating simultaneous increases in open-circuit voltage (Voc) and short-circuit current (Isc/Jsc). In the absence of DCA (0 mM), the curve exhibits a Voc of approximately 0.76 V and a maximum current of about 0.19 mA, with a relatively narrow profile. As the DCA concentration increases to 1 mM, 2 mM, and 3 mM, the curve widens, with

Voc rising to approximately 1.16 V and the current increasing to nearly 0.30 mA. This shift demonstrates that DCA enhances the electron injection process from chlorophyll molecules into the TiO_2 conduction band while simultaneously suppressing electron recombination with the electrolyte. Visually, the 4 mM curve displays the largest area beneath the maximum power point, signifying the highest power output and DSSC efficiency at this concentration. This aligns with the efficiency data, which showed an increase from 0.519% at 0 mM to approximately 1.533% at 4 mM, identifying 4 mM as the optimum DCA concentration for this chlorophyll-based DSSC system [42,43].

At a DCA concentration of 5 mM, the I–V curve still exhibits a relatively high Voc, yet the curve narrows compared to the 4 mM case due to a reduction in photocurrent. This phenomenon indicates that excessive DCA addition begins to hinder the adsorption of chlorophyll molecules onto the TiO_2 surface, as DCA competes for the same active sites. Consequently, the number of dye molecules participating in light absorption decreases, leading to a drop in current density, even though electron recombination remains low. This trend aligns with recent reports stating that, while DCA acts as a co-adsorbent—reducing dye aggregation, improving charge separation, and enhancing both Voc and Jsc at optimal concentrations—excessively high concentrations can actually degrade performance by reducing dye loading on the semiconductor surface. A study by [2] demonstrated that adding a bile acid-based co-adsorbent improved DSSC photovoltaic parameters by mitigating dye aggregation, while research on porphyrin-based DSSCs by Kumar and Ramasubbu (2022) [43] reported that DCA enhanced Voc, Jsc, fill factor, and efficiency up to an optimal concentration, beyond which performance declined due to adsorption competition. The results for this chlorophyll-based DSSC reveal a similar mechanism, reflecting a balance between enhanced electron transfer and a reduced dye adsorption at excessively high DCA concentrations [43].

Overall, the obtained plots demonstrate that DCA functions as both a molecular spacer and a surface passivating agent. DCA enhances the orderliness of dye adsorption, suppresses aggregation, improves electronic alignment at the dye/TiO_2 interface, increases electron injection efficiency, and reduces charge recombination. Collectively, these mechanisms improve Voc, Isc, Jsc, Pout, and PCE, with optimal values observed at a concentration of 4 mM. Thus, these findings highly align with modern DSSC theory, which posits that the control of molecular and interfacial structures is a key factor in enhancing the performance of dye-sensitized solar cells [12,22,24].

4. Conclusion

Extraction of papaya leaf chlorophyll using MAE showed that acetone was more effective than ethanol. The best results were obtained with acetone at an extraction time of 2 minutes, resulting in a total chlorophyll content of 12.024%, chlorophyll a of 7.342%, and chlorophyll b of 4.681%. The addition of Deoxycholic Acid (DCA) improved the performance of the papaya leaf chlorophyll-based DSSC stabilized with 3% $NaHCO_3$, with the optimum concentration of 4 mM yielding an output power of 1.35×10^{-4} W and an efficiency of 1.533%, representing an increase of approximately 195.4% compared to the control. Increasing the DCA concentration above the optimum level resulted in decreased performance due to adsorption competition between DCA and chlorophyll molecules on the TiO_2 surface.

Abbreviations

Not applicable

Data Availability Statement

Data supporting this study will be made available on request.

Credit Authorship Contribution Statement

Rukmi Sari Hartati: conceptualization, methodology, conceptual, translator, writing and editing. **Kadek Amerta Yasa**: conceptual, methodology, supervision, validation. P**oppy Diana Sari**: visualization, formal analyses, validation. **Fitriyah Nur Indahsari**: Resources, project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of Use of AI in the Writing Process

The author(s) used Deepl translator and Quillbot during the preparation of this manuscript to improve grammar, paraphrase text, and enhance clarity. After using the tool/service, the author(s) carefully reviewed and edited the content and take full responsibility for the content of the publication.

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