Science and Technology Indonesia
e-ISSN:2580-4391 *p*-ISSN:2580-4405
Vol. 11, No. 2, April 2026

Research Paper

Effect of pH on Brazilin Extraction from Sappanwood (*Caesalpinia sappan* L.) and Its Impact on the Efficiency of Natural Dye-Sensitized Solar Cells (DSSCs)

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Abstract

Dye-sensitized solar cells (DSSCs) are a sustainable photovoltaic technology for addressing the global energy crisis through the conversion of solar energy using photosensitive dyes. This study aims to investigate the effect of pH variation during extraction on the optical, electrochemical, and photovoltaic characteristics of brazilin dye from sappanwood (*Caesalpinia sappan* L.) for DSSC applications. Brazilian extraction was performed using Microwave-Assisted Extraction (MAE) with pH conditioning from 2 to 12. UV-Vis spectroscopy showed an increase in light absorbance at 400–800 nm. The pH 8 dye exhibited a maximum absorption peak at 444.59 nm due to the formation of a quinoidal base through partial deprotonation of the hydroxyl (−OH) group. FTIR characterization confirmed the chemical structure of the dye with characteristic absorption spectra of broad bands at 3000–3500 cm^{-1} for the phenolic hydroxyl group and peaks at 2800–3000 cm^{-1} for aromatic C−H stretching vibrations, as well as aromatic C=C and C=O stretching vibrations at 1600–1400 cm^{-1}. Energy band gap analysis revealed that the dye at pH 2–12 has an energy gap range of 0.1788–0.5355 eV. Optimizing the extraction pH revealed that pH 8 yields the most effective dye performance, resulting in a peak DSSC efficiency of 2.17%, a minimal charge transfer resistance of 100 Ω, and the narrowest energy bandgap at 0.1788 eV. Weakly basic conditions enhance dye molecule conjugation, strengthen bonding with TiO_2, and optimize the overall charge transfer process. The research findings confirm the potential of optimizing natural dye extraction conditions as a strategy to enhance DSSC efficiency in a sustainable and environmentally friendly manner.

Keywords

Dye-Sensitized Solar Cells (DSSCs), Photovoltaic, Brazilin, *Caesalpinia sappan* L., pH Variation, Efficiency

Received: 6 August 2025, Accepted: 24 December 2025
https://doi.org/10.26554/sti.2026.11.2.378-388

1. INTRODUCTION

Energy serves as the foundation of all human activities; however, its increasing scarcity poses significant global challenges. Most of the energy used today comes from non-renewable fossil fuels, a situation exacerbated by the continuously rising global demand for electricity, which is projected to increase by more than 3% per year (Wu et al., 2021). Continued reliance on fossil fuels leads to severe environmental consequences and raises sustainability concerns due to the depletion of non-renewable resources (Kusumawati et al., 2023; Arkan et al., 2024). Renewable energy is a strategic solution to address future fossil fuel scarcity, with solar energy being the most abundant source. By 2050, solar energy is expected to reach a potential capacity of approximately 150.73 PWh and supply over a quarter of the world's electricity demand (Holechek et al., 2022; Syafina and Oluleye, 2024). To optimize the utilization of solar energy, efficient conversion systems such as solar cells are required.

Dye-sensitized solar cells (DSSCs) are a promising third-generation solar cell technology due to their low production costs, simple manufacturing process, abundant availability of materials, and potential for environmentally friendly applications (Kusumawati et al., 2024b). DSSCs generate electricity from sunlight by utilizing semiconductor materials and operating based on the excitation of photosensitizer molecules (Moharam et al., 2021; Rahmawati et al., 2025). Recent advances have demonstrated that novel plant-based dyes can enhance DSSC performance, achieving power conversion efficiencies over 4% (Nasyori et al., 2024a). The main components of DSSCs include the working electrode, dye or sensitizer, electrolyte, and counter electrode, each of which plays a critical role in determining system efficiency. The electrolyte, as a key component, significantly influences DSSC performance; however, the commonly used liquid electrolytes have drawbacks such as leakage issues and limited lifespan, which impact long-term stability. o overcome these challenges, polymer-based electrolytes like polyvinylidene fluoride (PVDF) membranes have been introduced due to their excellent ionic conductivity, mechanical strength, flexibility, resistance to leakage, and enhanced durability over time (Kusumawati et al., 2024a).

Photosensitizers are important components that greatly influence the performance of DSSCs through their ability to inject electrons into the conduction band of semiconductors. Inorganic dyes particularly ruthenium(II) based complexes such as N3, N719, and black dyes are widely recognized as the most efficient sensitizers in dye-sensitized solar cells, delivering power conversion efficiencies in the range of 10–12%. However, their practical use is hampered by high material costs, limited availability, potential toxicity, and complex synthesis/purification procedures (Vallejo et al., 2025). The shift toward metal-free, natural dye-sensitized solar cells aligns with current trends in sustainable energy conversion (Malhotra et al., 2024). Natural dyes have emerged as a promising alternative due to their environmental compatibility, abundance, cost-effectiveness, and ability to absorb light with greater design flexibility compared to synthetic dyes (Mejica et al., 2022; Puspitasari et al., 2023).

Among various natural dyes, brazilin derived from sappan wood (*Caesalpinia sappan* L.) shows excellent potential with strong absorption in the visible light range and electron donation capability through its hydroxyl and carbonyl functional groups. The molecular structure of brazilin enables effective π-electron delocalization, facilitating enhanced light harvesting and electron transfer processes essential for high-performance DSSCs. In previous research, Amin et al. (2025) analyzed the main ions in sappan wood extract, which play an important role in influencing molecular interactions in DSSCs. This reinforces the significance of our research in the context of characterizing the chemical properties of extracts as natural dyes. Amogne et al. (2020) demonstrated that in anthocyanin-based dyes, extraction conditions, particularly pH and temperature, significantly influence the molecular structure, optical properties, and binding capacity of natural dyes, which can affect DSSC efficiency. Sikder et al. (2023) also showed that in flavonoid compound studies, extraction parameters can alter the conjugation system and energy levels of natural dyes. According to Estiningtyas et al. (2023), modifying the extraction pH influences the deprotonation of phenolic groups in brazilin, thereby altering its conjugated system and energy levels. The highest DSSC efficiency, 2.71%, was achieved using a combination of beetroot dye in ethanol and turmeric in distilled water under acidic conditions. Mohammadian et al. (2024) showed that slightly basic conditions can promote bathochromic shifts and enhance dye-semiconductor interactions through improved electronic coupling. Zakiyah et al. (2024) demonstrated that blending sappanwood and mangosteen extracts resulted in an energy efficiency of 1.389 eV. Rahmawati et al. (2025) reported that a ternary combination of natural dyes extracted from *Caesalpinia sappan* L., *Dracaena angustifolia*, and *Clitoria ternatea* L. achieved the highest solar cell efficiency, reaching 3.24%.

Although studies on the performance of brazilin in dye-sensitized solar cells have been conducted, there are still gaps regarding the relationship between extraction pH, electron density distribution, and various molecular forms of brazilin. Additionally, while previous studies have shown that increasing brazilin concentration can enhance photovoltaic performance, the understanding of pH-dependent molecular behavior and its direct correlation with DSSC efficiency has not been explored. This study aims to address these gaps by systematically investigating the influence of extraction pH on DSSC efficiency. Characterization was performed using UV-Vis spectroscopy, FTIR, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) to evaluate the pH effect on dye structure, energy level alignment, and charge transfer behavior. These findings are expected to provide fundamental insights into pH-controlled molecular engineering of brazilin to enhance DSSC performance, as well as contribute to the development of environmentally friendly and cost-effective photovoltaic technology.

2. EXPERIMENTAL SECTION

2.1 Materials

The materials of this study included Dimethylacetamide (DMA c) (≥99% purity; Merck, Germany), Acetone (CH_3COCH_3) (≥99.5% purity; Sigma Aldrich, USA), Ethanol (C_2H_6O) (≥99% purity; Merck, Germany), Propylene carbonate (99.7% purity; Sigma-Aldrich, USA). PVDF (Poly(vinylidene fluoride) (powder, Mw 534,000; Sigma-Aldrich, France) and PEG-1000 (Propylene glycol) (99% purity; Merck, Germany). HNO_3 (≥99.9% purity; Sigma-Aldrich, Singapore), Hydrochloric Acid (HCl) (≥99% purity; Merck, Germany) and Sodium Hydroxide (NaOH) (≥99% purity; Sigma Aldrich, USA). TiO_2 (9≥9% purity; Merck, Germany), KI (99% purity; Merck, Germany), and Iodine (≥99.8% purity; Smart-Lab, Indonesia). Anhydrous EC (99% purity; Merck, Germany), Tween 80 (≥99.8% purity; Smart-Lab, Indonesia). FTO glass (resistivity $10\ \Omega$) was produced by XinYu Xu Tking Glass Co, Ltd in China. *Caesalpinia sappan* L. was purchased from a local market (Surabaya, Indonesia).

2.1.1 Preparation of Natural Photosensitizer

The organic photosensitizer extraction was carried out using the maceration technique, adopting a procedure similar to that employed by Estiningtyas et al. (2023). The natural dye, sappan wood (*Caesalpinia sappan* L.), was obtained and washed with water until clean. The extraction process was then carried out using ethanol as a solvent at a ratio of 1:10 (sample:solvent). In this study, the Microwave-Assisted Extraction (MAE) method was employed, which had previously shown promise in enhancing pigment yield and stability. Optimization of temperature and ethanol concentration in MAE systems has shown a significant impact on the recovery of antioxidant compounds (Cavalluzzi et al., 2022). Microwave-Assisted Extraction (MAE) is a new technology reported to be effective in extracting bioactive compounds from various natural sources due to its ability to rapidly heat the extraction matrix, leading to rapid product extraction. MAE has been widely applied to extract phytochemicals efficiently due to its rapid energy transfer mechanism (Ahmad et al., 2021). The filtrate was then filtered and varied by adding HCl and NaOH at different pH levels: pH 2; pH 4; pH 6; pH 8; pH 10; and pH 12. The extract obtained through maceration was concentrated using a Buchi R-300 rotary evaporator. The resulting natural dye concentrate was subsequently stored at 20–25°C, making it ready for use as a photosensitizer in DSSC applications.

2.2 Preparation of TiO_2 Paste

TiO_2 paste was formulated by mixing 0.80 g of TiO_2 with 0.32 g of PEG-1000, 1.6 mL of Tween-80, and 0.2 mL of 0.1 M HNO_3. The mixture was stirred for 30 minutes at 100 rpm using a NESCO LAB MS-H280-Pro magnetic stirrer until homogeneous. The resulting paste was then applied to precleaned FTO glass substrates using the doctor blade method and sintered at 450°C for 60 minutes, following the procedure adapted from (Kusumawati et al., 2024b).

2.3 Preparation of PVDF NF Membrane

The PVDF membrane was fabricated via the electrospinning method, in accordance with the protocol outlined by Kusumawati et al. (2024b). An 18% (w/v) PVDF solution was prepared by dissolving the polymer in a 3:2 solvent mixture of DMAc and acetone, using a magnetic stirrer at 65°C and 270 rpm for 12 hours. The 18% (w/v) PVDF solution was then fabricated using the electrospinning casting technique, conducted for 5 hours under a constant voltage of 15 kV, with a flow rate of 1 mL/hour and varying distances between the needle and collector at 5 cm, 10 cm, and 15 cm (Kusumawati et al., 2023; Kurniawan et al., 2025).

2.4 Preparation of Electrolyte

The electrolyte was prepared by dissolving 0.09 g of I_2, 0.60 g of KI, 4.00 g of PC, and 4.00 g of EC using magnetic stirring at 100 rpm for one hour (Kusumawati et al., 2023). To maintain its photostability, the solution was then stored in a light-protected, opaque container for later use in device fabrication.

2.5 Fabrication DSSC

Following the sintering step, the TiO_2-based photoanode was soaked in 10 mL of the natural dye extract for a period of 24 hours to facilitate dye adsorption. Simultaneously, the electrospun PVDF membrane was trimmed to a size of 2.0 cm × 1.5 cm and subsequently immersed in 1 mL of the prepared electrolyte solution to ensure full saturation. The electrode dimension (2.0 cm × 1.5 cm) was adopted from previous DSSC fabrication protocols (Rahmawati et al., 2025) to ensure comparability with reported efficiencies. This standard size provides sufficient active surface area for dye adsorption and photocurrent generation while maintaining reproducible cell assembly. A carbon layer derived from wax soot was then deposited onto the conductive surface of the FTO glass. The DSSC circuit was assembled in an FTO/$TiO_2$$^+$Brazilin/PVDF NF+Electrolyte/Carbon/FTO configuration to form a sandwich structure, as shown in Figure 1.

The fabrication process comprises multiple sequential steps. The working electrode is prepared by initially cleaning the FTO substrate, followed by the application of TiO_2 paste using the doctor-blade technique. The coated substrate is subsequently sintered at 450°C, allowed to cool, immersed in the natural dye extract, and air-dried. For the counter electrode, the FTO glass undergoes a similar cleaning procedure, after which a platinum catalyst is applied and thermally treated through heating and cooling stages. The previously fabricated PVDF membrane is immersed in the electrolyte solution to enable ion absorption. Assembly of the DSSC is completed by aligning the working electrode, electrolyte-soaked membrane, and counter electrode in sequence, and securing them firmly using clamps.

2.6 Characterization Techniques

Characterization includes UV-Vis spectroscopy in the wavelength range of 300–800 nm to determine the absorption spectrum of natural dyes. A Perkin Elmer Spectrum Two FTIR spectrometer was used to determine the functional groups in natural dyes. The energy bandgap of the natural dye photosensitizers was determined through cyclic voltammetry analysis, employing a 797 VA Computrace Metrohm Voltammetry system to record oxidation and reduction currents. Concurrently, variations in the current and voltage output of the DSSC devices were measured using a Krisbow KW08-267 digital multimeter to assess their electrical performance.Electrochemical impedance spectroscopy (EIS) was also used to measure charge transfer resistance in the range of 0.1 Hz–100 kHz using the Gamry Reference 3000 Electrochemical Impedance Spectroscopy (Kusumawati et al., 2023).

3. RESULTS AND DISCUSSION

3.1 Active Compounds of Sappanwood Extract

Caesalpinia sappan L. is a rich source of phytochemicals, with brazilin and its oxidized derivative brazilein recognized as the primary homoisoflavonoids responsible for the reddish coloration of sappanwood extract. Both compounds possess extended π-conjugation and visible light absorption, making them suitable as natural photosensitizers in DSSCs. As summarized in Table 1, brazilin and brazilein serve as major homoisoflavonoids and main chromophores with strong visible absorption (Vij et al., 2023). The principal chromophores of *Caesalpinia sappan* L. are brazilin and its oxidized derivative, brazilein. Their 2D chemical structures are presented in Figures 2(a) brazilin and (b) brazillein along with identifiers to facilitate reproducible structural rendering.

Brazilin is a homoisoflavonoid (neoflavonoid) bearing three phenolic hydroxyls; oxidation at the benzylic position generates brazilein with a conjugated carbonyl, shifting the absorption toward longer wavelengths. This interconversion underlies the extract's bathochromic shift and the improved visible-region

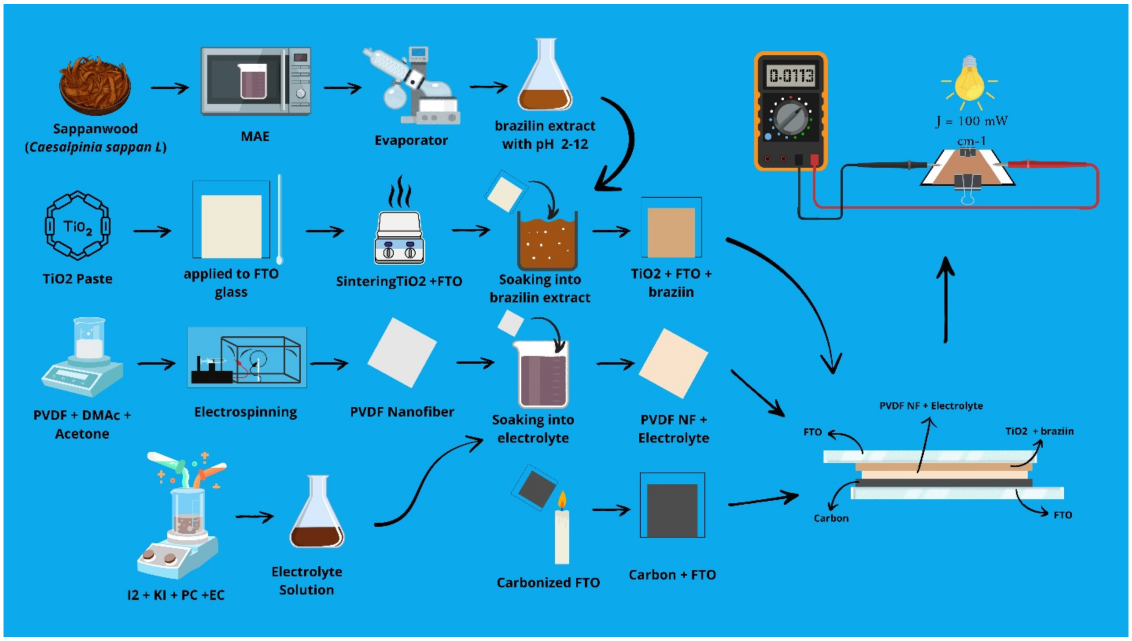

Figure 1. Fabrication of DSSC Circuit

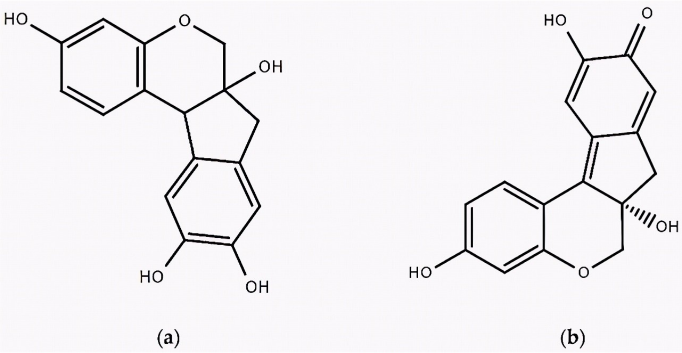

Figure 2. Structure of (a) Brazilin and (b) Brazilein (Vij et al., 2023)

absorption often observed after controlled oxidation/alkalization in dye applications.

In addition to these major chromophores, numerous other active compounds have been identified in the extract, as detailed in Table 1. Secondary homoisoflavonoids including chalcones and protosappanins A–D function as antioxidants and structural stabilizers (Vij et al., 2023). A comprehensive GC-MS analysis of methanolic extract identified 33 bioactive constituents, encompassing phenolic acids, flavonoids, steroids, and alkaloids (Wirawati et al., 2023). Table 1 further shows that two pure antioxidant molecules, alpinetine and 3-deoxysappanone B, have been successfully isolated and characterized using LC-MS/MS techniques (Yodha et al., 2021). Additionally, flavonoid glycosides and triterpenoids have been reported in phytochemical profile reviews, which may contribute synergistically to the extract's antioxidant and functional properties (Wirawati et al., 2023). Overall, while brazilin and brazilein remain the dominant sensitizers as indicated in Table 1, other minor constituents may contribute to dye stability, antioxidative support, and interfacial electron transfer in DSSCs.

Table 1. Active Compounds of *Caesalpinia sappan* L.

Compound	Activity	Reference
Brazilin, Brazilein	Major homoisoflavonoids, main chromophores, strong visible absorption	(Vij et al., 2023)
Chalcones, Protosappanin A–D	Secondary homoisoflavonoids, antioxidant, structural stabilizer	(Vij et al., 2023)
33 bioactive compounds (phenolics, flavonoids, steroids, alkaloids)	Identified by GC-MS in methanolic extract	(Wirawati et al., 2023)
Alpinetine; 3-Deoxysappanone B	Pure antioxidants isolated by LC-MS/MS	(Yodha et al., 2021)
Flavonoid glycosides, Triterpenoids	Reported in reviews of phytochemical profile	(Wirawati et al., 2023)

Besides organic compounds, the electrolyte ion composition of sappanwood extract also plays a role in its performance as a DSSC dye. Amin et al. (2025) reported through ion chromatography that the extract contains dominant cations such as Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, with Ca^{2+} concentration reaching 83.73 mg/kg. The presence of these cations is significant because they can interact with TiO_2 surfaces via adsorption and complexation, potentially improving dye anchoring, enhancing interfacial stability, and facilitating charge transfer.

This suggests that the overall photovoltaic performance of DSSCs sensitized with sappanwood extract is influenced not only by its organic chromophores (brazilin and brazilein) but also by its ionic composition, which contributes to interfacial electron dynamics.

3.2 UV-Vis Spectroscopy Analysis

Natural dyes serve a crucial function in enhancing visible light absorption on TiO_2 substrates in dye-sensitized solar cells (DSSCs). Compared to synthetic dyes, natural alternatives offer several advantages, such as widespread availability, straightforward extraction processes, higher molar absorptivity, lower production costs, non-toxic properties, and environmental degradability. (Mejica et al., 2022; Puspitasari et al., 2023). This study evaluates the effect of pH conditions on brazilin dye extracted from sappanwood (*Caesalpinia sappan* L.) as a potential natural dye for DSSC applications through spectrophotometric analysis in the visible light range of 400–800 nm.

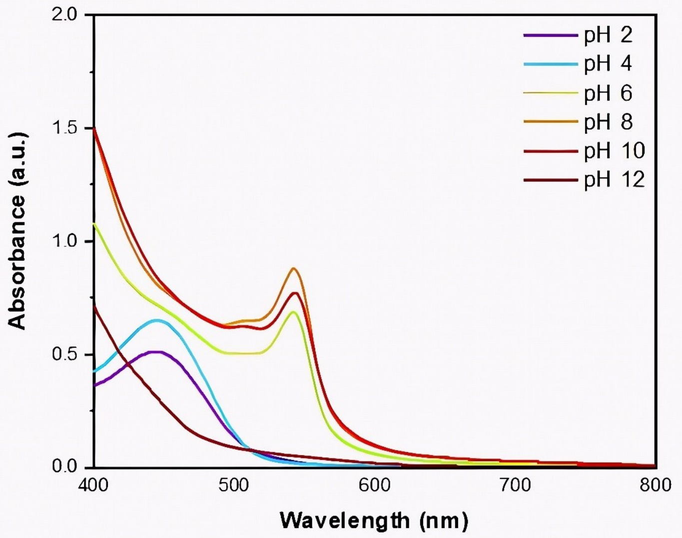

Figure 3. UV-Vis Absorption Spectra of Brazilin Extracts from Sappanwood at Different pH Conditions

Optical property analysis was conducted on Brazilin dye extracted using ethanol as a solvent via microwave-assisted extraction (MAE) at 280 W for 15 minutes. This method is highly effective in maintaining the structural integrity of the Brazilin molecule under various pH conditions, as indicated by its characteristic absorption patterns. The UV-Vis absorption spectra of brazilin extracts across the pH range of 2–12 exhibit varying spectroscopic profiles corresponding to structural transformations under different acidic and basic conditions, as shown in Figure 3.

Spectrophotometric data show a significant bathochromic shift with a peak wavelength at 443.77 nm for pH 2, indicating the dominance of the flavylium cation, followed by an initial deprotonation transition at 444.59 nm for pH 4 and 541.90 nm for pH 6 in the quinoidal base form through partial deprotonation of the $-OH$ group, reaching an optimal condition at 543.00 nm for pH 8 and at 542.27 nm for pH 10 with further deprotonation to form a carbinol pseudobase and a chalcone at pH >10, which undergoes irreversible degradation. At pH 12, no peak is detected in the 400-800 nm range, indicating molecular degradation. The bathochromic shift in the 400–800 nm range from acidic to basic pH indicates a significant extension of the π-electron conjugation system.

This spectral shift phenomenon can be explained by changes in the protonation level of the phenolic hydroxyl groups in the brazilin structure. Under acidic pH conditions, the hydroxyl groups tend to remain protonated, limiting the formation of resonance structures and electron delocalization throughout the chromophore. As pH increases, deprotonation occurs, forming phenoxide anions that participate in broader conjugation, thereby reducing the energy gap for electronic transitions (Yuniati et al., 2023). The highest absorbance was recorded at pH 8 with the maximum absorbance value, indicating increased electron delocalization and π conjugation essential for effective photon capture. This pH-dependent absorption pattern differs from the concentration-dependent absorption of brazilin, which follows the Lambert-Beer law, due to the formation of different molecular structures at different pH values through gradual deprotonation (Estiningtyas et al., 2023; Mohammadian et al., 2024).

From a photovoltaic application perspective, brazilin extract conditioned at pH 8 exhibits optimal light absorption capability, followed by pH 10 and pH 6. The broad absorption pattern in the 400–800 nm range exhibited by pH 6–8 samples provides advantageous visible spectrum coverage, with optimal overlap with the solar irradiance spectrum, which is particularly beneficial for DSSC applications. This spectral shift directly impacts the light-harvesting capability of brazilin in DSSC applications, as it enables more efficient photon capture across various wavelengths, potentially enhancing the photovoltaic conversion efficiency of solar cell systems. This finding is supported by Purba et al. (2024), who reported strong UV-Vis absorbance of Sappanwood extract in the 396–478 nm range, attributed to its high phenolic and conjugated content-highlighting its suitability for visible-spectrum sensitization in DSSCs.

3.3 FTIR Spectroscopy Analysis

Fourier Transform Infrared (FTIR) spectroscopy analysis was performed to identify the functional groups present in brazilin extract from sappanwood (*Caesalpinia sappan* L.). The FTIR spectrum in Figure 4 shows structural consistency across all pH conditions (pH 2–12), indicating that the core molecular structure of brazilin remains intact despite pH variations, with transmission measurements recorded in the wavenumber range of 4000–500 cm^{-1}. All spectra exhibit similar absorption patterns and peak positions, confirming the structural stability of the brazilin chromophore under acidic and basic conditions. This consistency is crucial for DSSC applications, as it ensures the dye retains its essential properties under various operational conditions.

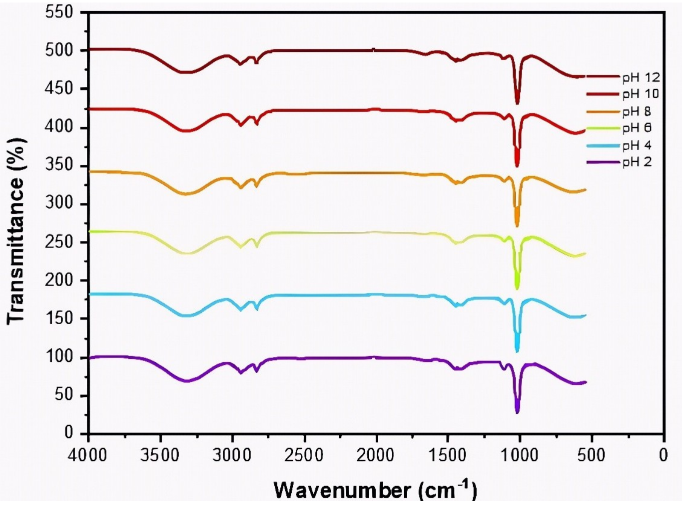

Figure 4. FTIR Spectra of Brazilin Extracted from Sappanwood at Various pH Values

The FTIR spectrum reveals distinct absorption regions, notably a broad band between 3000–3500 cm^{-1}, which is attributed to O–H stretching vibrations of phenolic hydroxyl groups in the brazilin molecule. The broadness of this peak suggests the involvement of intermolecular hydrogen bonding interactions within the dye structure. The absorption peak in the 2800–3000 cm^{-1} range represents the aromatic C−H stretching vibrations of the benzene ring in the brazilin structure, while the absorption band at 1600–1400 cm^{-1} corresponds to the aromatic C=C and C=O stretching vibrations, which are characteristic of the quinoidal and flavylium forms of brazilin. Additionally, strong absorption around 1000 cm^{-1} indicates C−O stretching vibrations from the phenolic group, which plays a crucial role in the dye binding mechanism on the TiO_2 surface.

Comparative FTIR spectrum analysis of brazilin shows that when the pH of the natural dye is modified, they coexist without forming new chemical bonds, as evidenced by the absence of significant new peaks or substantial shifts in the existing absorption bands. This chemical compatibility indicates excellent stability under varying pH conditions, a desirable property for DSSC applications. These findings highlight the potential of brazilin from sappanwood (*Caesalpinia sappan* L.) as a natural sensitizer in dye-sensitized solar cell technology and other applications where chemical stability under varying pH conditions is an advantage. The identified functional groups align with the characteristic molecular structure of brazilin, marked by aromatic rings, hydroxyl groups, and conjugated double bonds that contribute to its distinctive spectroscopic properties and functional diversity.

The consistent functional group profile across various pH conditions demonstrates that brazilin retains its essential chromophore properties required for light absorption in solar cell applications. The identification of O−H and C−O stretching vibrations signifies the existence of dihydroxyl functional groups, which facilitate the dye's interaction with the TiO_2 surface through hydrogen bonding or chelation mechanisms. The aromatic system, indicated by the C=C stretching band, ensures effective π electron conjugation for photon absorption and charge transfer processes. These vibrational features align with those reported by Arsyad et al. (2024), who observed similar FTIR spectra in brazilein extracts and demonstrated that such groups play a key role in enhancing DSSC performance-especially when coupled with ZnO nanoparticles.

3.4 Cyclic Voltammetry Analysis

In an effort to improve the overall efficiency of DSSCs and optimize the performance of natural dyes as photosensitizers, the parameter that must be met is that the energy gap of the dye is narrower than that of the TiO_2 semiconductor. The effectiveness of the extracted dye increases as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases. The dye's ability to regenerate indicates the ease of electron transfer from the I^- or I_3^- electrolyte to the HOMO band of the material. This is related to the fact that dye electrons can be more easily driven from the valence band to the conduction band when they have a sufficiently small amount of energy. TiO_2 influences the conduction band, aligning its effect with the energy level of the dye molecule's LUMO and facilitating electron injection. Specifically, the anatase phase has a band gap energy of 3.2 eV, while the rutile phase shows a slightly lower value of 3.0 eV. The determination of the dye's band gap energy defined in Equations (1)-(3) (Setiarso et al., 2023).

$$E_{\mathrm{HOMO}} = -\left(E_{\mathrm{ox}} + 4.40\right)\ \mathrm{eV} \tag{1}$$

$$E_{\mathrm{LUMO}} = -\left(E_{\mathrm{red}} + 4.40\right)\ \mathrm{eV} \tag{2}$$

$$E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{3}$$

The energy band gap values observed across various pH levels indicate that brazilin extracted from sappanwood (*Caesalpinia sappan* L.) satisfies the criteria necessary for functioning as an effective sensitizer in DSSC applications. The LUMO energy levels of the dyes are substantially more positive than the TiO_2 conduction band edge at −4.0 eV, a crucial factor that facilitates efficient electron injection from the excited dye molecules into the semiconductor.

As presented in Table 2, the energy gap values across different pH conditions range from 0.1788 eV to 0.5355 eV, with

Table 2. The HOMO, LUMO, and Band Gap Values for Brazilin Extracted from Sappanwood at Various pH Values

Dye (various pH)	HOMO (eV)	LUMO (eV)	Eg (eV)
pH 2	-3.2026	-2.7089	0.4937
pH 4	-3.2175	-2.7469	0.4706
pH 6	-4.0145	-3.6183	0.3962
pH 8	-4.2595	-4.0807	0.1788
pH 10	-4.1145	-3.9160	0.1985
pH 12	-3.1904	-2.6549	0.5355

the most favorable outcome observed at pH 8, where the lowest bandgap of 0.1788 eV indicates enhanced performance. This optimal pH condition indicates the suitability and stability of the dye extract for DSSC applications. A narrower energy gap facilitates more efficient electron transfer, which is crucial for the long-term performance of DSSCs. A reduced bandgap between the valence and conduction bands facilitates electron mobility, thereby improving the material's overall electrical conductivity. Consistent with this, Sikder et al. (2023) emphasize that natural dyes with a well-aligned LUMO above TiO_2 conduction band and reduced Eg values achieve significantly greater electron transfer rates and overall solar cell performance improvements. The pH 8 condition displays optimal characteristics for DSSC applications with the smallest band energy gap, allowing for more effective electron transfer and improved photovoltaic performance.

3.5 Photovoltaic Studies

The performance of the DSSC system was evaluated by measuring open-circuit voltage (Voc), short-circuit current (Jsc), fill factor (FF), and power conversion efficiency (η) under illumination intensity of 100 mW/cm^2 using a multimeter. The overall performance was quantified using the fill factor (FF), calculated through Equation (4), and efficiency (η), determined by Equation (5), following the method outlined by Kusumawati et al. (2024a). These parameters include Vmax as the maximum output voltage, Imax as the maximum output current, Isc as the short-circuit current, Voc as the open-circuit voltage, and Pin as the system input power.

$$\mathrm{FF} = \frac{V_{\max} \times I_{\max}}{V_{\mathrm{oc}} \times I_{\mathrm{sc}}} \tag{4}$$

$$\eta = \frac{\mathrm{FF} \times V_{\mathrm{oc}} \times I_{\mathrm{sc}}}{P_{\mathrm{in}}} \tag{5}$$

This research assessed the current–voltage (I–V) characteristics of DSSCs sensitized with brazilin extracted from sappanwood (*Caesalpinia sappan* L.) at different pH levels. The evaluation focused on key photovoltaic parameters including open-circuit voltage (Voc), short-circuit current (Isc), and fill factor (FF). The influence of brazilin as a natural photosensitizer on DSSC performance is illustrated in the I–V curves (Figure 5) and further detailed in the photovoltaic data summarized in Table 3. The effectiveness of brazilin dye from sappanwood shows promising potential as a photosensitizer in DSSC technology, with a significant ability to capture photons at wavelengths suitable for the DSSC energy conversion mechanism and convert photons into electrical energy. Variation in pH plays a role in expanding the absorption range of sunlight, potentially increasing the overall efficiency of the DSSC, demonstrates favorable chemical and photochemical stability. A similar pH-dependent shift in DSSC performance was reported when using a range of natural dyes under varying annealing conditions (Nasyori et al., 2024b).

Table 3. The DSSC Photovoltaic Parameter Values for Brazilin Extracted from Sappanwood at Various pH Values

Dye (various pH)	V_{oc} (mV)	I_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
pH 2	184	0.0089	24.34	0.54
pH 4	260	0.0096	15.97	0.83
pH 6	302	0.0106	12.41	1.07
pH 8	576	0.0113	6.11	2.17
pH 10	333	0.0109	10.99	1.21
pH 12	54	0.0072	102.41	0.13

Of the six pH variations tested, the observed efficiency order is pH 8 (2.17%) > pH 10 (1.21%) > pH 6 (1.07%) > pH 4 (0.83%) > pH 2 (0.54%) > pH 12 (0.13%). The pH 8 condition demonstrated optimal performance with I_{sc}, V_{oc}, FF, and photoconversion efficiency (η) values of 0.0113 mA/cm^2, 576 mV, 6.11%, and 2.17%, respectively. This achievement indicates that the dye extract at pH 8 maintains stability and effectiveness under DSSC operating conditions.

For clarity, the photovoltaic efficiencies of natural dye-based DSSCs reported in the literature were compared with the present study. The results are summarized in Table 4.

As shown in Table 4, compared to other reported natural dye-based DSSCs, the efficiency achieved in this study (2.17%) demonstrates several advantages. First, unlike blended or multi-dye systems which require complex optimization, our work uses a single natural dye with optimized pH, providing a simpler and more reproducible system. Second, the optimized pH 8 condition not only enhances dye stability but also results in the lowest band gap (0.1788 eV) and minimal charge transfer resistance (100 Ω), which are favorable for electron injection and long-term device stability. Thus, although the efficiency is slightly lower than multi-dye blends, the simplicity, stability, and mechanistic insights gained in this study represent a significant advantage for the rational design of sustainable DSSCs.

The influence of extraction pH is critical, as it determines dye adsorption and stability on the TiO_2 surface. Consistent

Table 4. Comparison of Natural Dye-Based DSSC Efficiencies Reported in Literature

Dye source	Condition (pH/treatment)	η (%)	Reference
Caesalpinia sappan L. extract (this research)	pH 8 (optimized)	2.17	This research
Turmeric + sappanwood (double dye)	Neutral pH	2.09	(Estiningtyas et al., 2023)
Turmeric + beetroot (double dye)	Acidic pH	2.71	(Estiningtyas et al., 2023)
Sappanwood + pandan + telang (triple blend)	Optimized blend	3.24	(Rahmawati et al., 2025)
Anthocyanin dyes (berry extract)	Alkaline pH (10–12)	< 1.0	(Okello et al., 2022)

with our findings, Estiningtyas et al. (2023) showed that acidic pH improved efficiency compared to neutral pH, while Okello et al. (2022) observed a decline in Jsc and overall efficiency at strongly alkaline pH (10–12) due to poor dye anchoring. Thus, pH 8 provides a favorable balance between stability and adsorption capacity, supporting efficient electron injection. Mechanistically, the improved performance at pH 8 can be attributed to better dye coverage and reduced charge recombination. Kim et al. (2024) demonstrated that higher dye loading on TiO_2 leads to enhanced Jsc and Voc, provided recombination is minimized. This condition explains why the optimized dye extract at pH 8 maintains stability and effectiveness under DSSC operating conditions.

This finding aligns with both our band gap analysis where the pH 8 extract showed the lowest band gap (0.1788 eV) and broader trends in natural dye DSSC research. Narrow band gaps enhance light absorption and accelerate electron transfer via extended π-conjugation, which is consistent with findings by Sikder et al. (2023). Moreover, recent modeling studies by Kumar and Patra (2023) demonstrated that natural dyes with $E_g < 1$ eV absorb predominantly in the visible spectrum, directly contributing to higher photovoltaic efficiencies. This consistency aligns with previous bandgap analysis, which showed that the dye at pH 8 has a smaller bandgap. A smaller bandgap value indicates faster electron transfer due to the increased number of conjugated chains. The bandgap data revealed that the dye at pH 8 has the smallest bandgap among all other pH variations, contributing to improved sunlight absorption performance and more efficient photon energy utilization.

The I-V curves show that pH 8 provides the best performance with a high open-circuit voltage and optimal current density. The pH 8 exhibits the most ideal curve characteristics with a combination of high Voc and adequate Jsc, resulting in the highest efficiency. The molecular structure of brazilin at pH 8 in the form of carbinol pseudobase facilitates optimal light absorption and efficient electron transfer to TiO_2. In addition, the increase in DSSC efficiency is also influenced by the optimization of TiO_2 thickness of 0.2 mm and the optimal PVDF NF polymer electrolyte membrane, as reported by Kusumawati et al. (2024a).

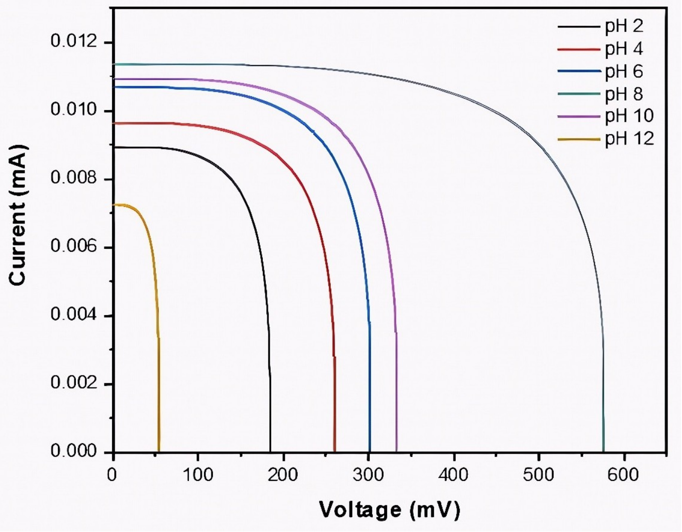

Figure 5. The I-V Curves Were Obtained for DSSCs Sensitized with Brazilin Extracted from Sappanwood at Varying pH Values

3.6 Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots from the EIS analysis presented in Figure 6 show the electrochemical impedance characteristics of brazilin dye from sappanwood (*Caesalpinia sappan* L.) at various pH variations, where each condition produces a different semi-circular diameter and is directly correlated with the charge transfer resistance in the system. The pH 12 shows the largest semi-circular diameter with a value reaching around 1800 Ω, indicating very high resistance and poor performance, while pH 8 and pH 10 show relatively small diameters with values around 400-600 Ω, indicating higher efficiency. A more detailed analysis reveals that the charge transfer resistance (Rct) reaches its lowest value at pH 8 (100 Ω), indicating the most efficient interfacial charge transport between the dye and TiO_2/electrolyte system, corresponding to the extreme conditions of pH 2 and pH 12, which show high Rct values (>700 Ω) with hindered electron mobility and increased recombination.

The high performance at pH 8 can be attributed to the better sensitizing ability of natural dyes, high surface coverage, and optimal redox potential adjustment under slightly alkaline conditions. Masud and Kim (2023) reported that optimal pH conditions facilitate stable interactions between dyes and TiO_2 substrates. Meanwhile, excessive acidity or alkalinity can disrupt the electronic structure of the dye or damage the TiO_2 layer, resulting in decreased DSSC performance as confirmed by Vij et al. (2023). Consequently, pH 8 achieves an optimal

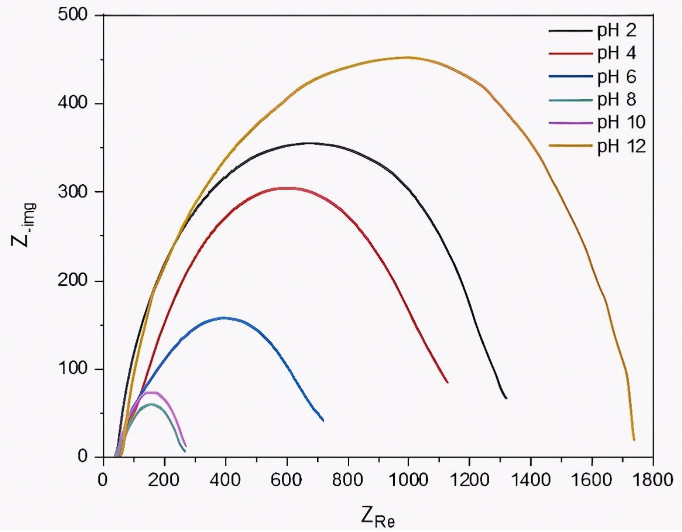

Figure 6. Nyquist Plots Obtained from EIS Measurements of DSSCs Sensitized with Brazilin Extracted at Various pH

balance between molecular stability, adsorption behavior, and charge kinetics, which is reflected in a combination of minimal charge transfer resistance and maximal photovoltaic efficiency, with a low Rct value reflecting fast electron exchange and fewer recombination losses at the TiO_2/dye/electrolyte interface.

4. CONCLUSIONS

The findings of this study demonstrate that natural dyes extracted from sappanwood (*Caesalpinia sappan* L.) serve as efficient photosensitizers for dye-sensitized solar cells (DSSCs). UV-Vis spectroscopy characterization revealed that the dye at pH 8 exhibits optimal absorption peaks at 444.59 nm due to the formation of a quinoidal base resulting from partial deprotonation of the hydroxyl (−OH) group. FTIR analysis verified the molecular structure of the dye, revealing distinct absorption bands: a broad region between 3000–3500 cm^{-1} corresponding to phenolic O–H stretching, peaks in the 2800–3000 cm^{-1} range for aromatic C–H stretches, and signals at 1600–1400 cm^{-1} indicating aromatic C=C and carbonyl (C=O) vibrations. The chemical stability of the dye was found to be excellent across a range of pH values, with no formation of new chemical bonds or significant shifts in absorption bands, indicating the desired compatibility for DSSC applications. Analysis of the energy bandgap revealed values ranging from 0.1788 to 0.5355 eV across pH levels 2 to 12. Optimal performance was observed at pH 8, where the dye exhibited the lowest bandgap (0.1788 eV), minimal charge transfer resistance (100 Ω), and the highest DSSC efficiency of 2.17%. Weakly basic conditions were found to enhance dye molecule conjugation, strengthen bonding with TiO_2, and optimize overall charge transfer. These findings confirm that optimizing natural dye extraction conditions is an effective strategy for sustainably enhancing DSSC efficiency, offering a potentially environmentally friendly alternative for future solar cell technology development.

5. ACKNOWLEDGMENT

The author gratefully acknowledges funding support from the Indonesian Ministry of Education, Culture, Research, and Technology, awarded through the national competitive research grant program.

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