

Review

Alternative Sources of Natural Photosensitizers: Role of Algae in Dye-Sensitized Solar Cell

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Abstract: In this paper, the potential of marine algae to act as sensitizers is systematically studied and presented. We aim to find a feasible financial strategy to enhance the global efficiency of dye-sensitized solar cells (DSSC). Algae are mainly composed of chlorophylls, carotenoids, flavonoids, and *Betalains*, which are essential pigments that confer unique characteristics that are required in natural sensitizers. Therefore, this review aims to unveil and understand the underlying mechanism between algae pigments and photoelectrodes and to conduct a comprehensive analysis to determine the effect of algae dye on light absorption efficiency and electron transport. The structural, morphological, optical, and electrochemical impedance properties are deeply analyzed, and we show the current opportunities for natural dyes to be used in energy technologies through DSSC. A comparison of several bibliographic sources dealing with DSSC based on algae provided a general overview of the improvements in factors such as the recombination times, the filling factor, and the Voc values. The contributions of this paper relate to the conversion efficiency and future applications in the DSSC field. Finally, this review exemplifies that the nature of the pigment affects the photophysical properties of the cell. Thus, this paper may contribute to future investigations of DSSC when choosing efficient natural dyes according to their optical and electronic properties. Therefore, this work provides the knowledge required to efficiently merge materials and dyes, in which photovoltaic energy systems' reproducibility and scalability still represent a challenge. Lastly, this document discusses the natural pigments' stability and the approaches to improve their chemical stability.

Keywords: algae; dye-sensitized solar cells; electrochemical impedance spectroscopy; natural pigments; optical properties



Citation: Armendáriz-Mireles, E.N.; Calles-Arriaga, C.A.; Pech-Rodríguez, W.; Castillo-Robles, A.; Rocha-Rangel, E. Alternative Sources of Natural Photosensitizers: Role of Algae in Dye-Sensitized Solar Cell. *Colorants* **2023**, *2*, 137–150. <https://doi.org/10.3390/colorants2010010>

Academic Editors: Nadia Barbero, Carlotta Pontremoli and Simone Galliano

Received: 14 February 2023

Revised: 27 February 2023

Accepted: 28 February 2023

Published: 17 March 2023



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1. Introduction

Depending on their color and characteristic wavelengths, natural dyes extracted from plants or fruits can enhance photon absorption to sensitize semiconductors [1,2]. Dye-sensitized solar cells (DSSC) are thin-film solar cells that use a dye to absorb sunlight and transform it into electrical power [3]. Algae, particularly microalgae, contain photosynthetic pigments called chlorophylls and carotenoids that can act as natural dyes in DSSC [4].

Solar energy represents a renewable source with great potential to change global energy towards more sustainable and economically viable technologies. Dye-sensitized solar cells (DSSC) are an attractive alternative due to their theoretical efficiency and low semiconductor cost [5]. Unlike perovskite solar cell technology [6–9], which is a promising strategy with high and competitive efficiencies, these devices are made of inorganic materials, and our work focuses on studying the pathway of the effects of the extracted dyes from natural sources, specifically from algae, and their behavior under controlled conditions.

Chlorophyll in algae is a chelate-type compound consisting of hydrogen, carbon, and a metal ion that binds to main molecules and with other elements such as oxygen and nitrogen. In photosynthesis, chlorophyll absorbs energy, turns carbon dioxide into carbohydrates, and converts water into oxygen. Through this process, the energy from the

sun is converted into a form that plants can absorb and use. The molecular structure is composed of a chlorine ring with an Mg center, several chains, and small hydrocarbons, depending on the type of chlorophyll source. The use of natural pigments comes from their increasing efficiency, which occurs when using colored dyes as photosensitizers, and they can collect light in the visible range of the spectrum to generate an electric current. While the usage of natural dyes as colorants is blooming in the food industry and in modern medicine, there is also an apparent growing interest in such natural chemical systems from the photonics community due to their π - π^* /conjugated electronic structures [10,11]. Owing to this intermolecular π - π^* transition, natural dyes exhibit significant absorption coefficients in the visible and near-infrared spectral range, which are conjugated with a high light-harvesting efficiency and potential photosensitizing applications in DSSC. The Grätzel solar cell, also known as a dye-sensitized solar cell [12,13], produces electricity via a photoelectrochemical principle, whereby it changes light energy into electrical energy. It consists of a semiconductor formed between a photosensitive anode and an electrolyte. The cell has desirable properties as it is low cost, easy to manufacture, semiflexible, semitransparent, or even transparent. In practice, the use of this cell shows certain disadvantages, such as the leak of the electrolyte or the anode instability under certain environmental conditions. However, they do not only have a high theoretical energy conversion efficiency compared with silicon-based solar panels, but they also improve the manufacturing price, which makes them a better candidate for mass distribution. Precisely, DSSC offers exciting possibilities in photovoltaics. Improving the charge transport through the metal oxide film, finding dyes with better absorption both in the visible and near-IR regions of the solar spectrum, and fabricating innovative materials for the scattering layer are some of the proposed ways to further improve the efficiency of DSSC. In the search for better dyes to sensitize cells, some studies [14–19] have focused on working with natural materials at nanometer scales.

For example, Ahmed M. Ammar et al. [18] studied three natural dyes: chlorophyll, anthocyanin, and onion extracted from different fruits and leaves, and then used them as sensitizers for dye-sensitized solar cells. The authors studied the UV–visible absorption and photoluminescence properties of the extracted dyes and concluded that chlorophyll gave the most extended lifetime and the highest possible efficiency among the dyes extracted.

Likewise, Can et al. [17] investigated the optical properties by using UV–Vis absorption and fluorescence measurements of two nanocyno molecules that were synthesized and used in the elaboration of DSSC. They group calculated the efficiency of the DSSC device and found that the bonding of different S donor atoms to the molecule had a little positive effect on the photovoltaic efficiency. Research has also been carried out whereby the authors combined dyes extracted from several natural sources, and modest cell efficiency results have been found to date [20–22].

Degradation is a significant problem when using dyes extracted from plants. In the search for more durable dyestuffs, some studies [23,24] used chitosan extracted from the shell of some crustaceans as dyes in the construction of DSSC and achieved cell efficiencies close to 10%, which is a low-efficiency value when compared to ruthenium-based sensitizers. Alternatively, using metals and minerals at the nanoscale as sensitizing media for DSSC has also been extensively studied [25–31].

Cerdá and Botasini [32] studied the red protein phycoerythrin extracted from Antarctic algae with spherical silver nanoparticles as cosensitizers in DSSC photoanodes. The research showed that the presence of the NPs helped to anchor the protein to the electrode surface, which improved the electron transport and also affected the long-term performance and stability of the assembled cells.

In this sense, DSSC are expected to fulfill several characteristics such as flexibility, harvesting efficiency [33], and efficient optical absorption [34]. Additionally, as in the applied materials, the nanoparticles significantly impact the cells [35,36]. In addition, pH and temperature eventually play an essential role in the size and morphology of the NP. Their synthesis plays a crucial role in their wide-spectrum applications, which differ from

industrial devices, electronics, and sensors [37,38]. Indeed, pigments extracted from algae represent an attractive alternative.

In fact, more than 30 million tons of algae are produced annually for industrial purposes, and part of this production (approx. 14 million tons) of a few species of red algae is used for hydrocolloids (agar and carrageenan) [39]. Likewise, the water-soluble light-harvesting phycoerythrin proteins found in cyanobacteria and red and blue-green algae have characteristics that make this protein a good natural-pigment candidate to study in the application of DSSC [40,41]. A key aspect is that free carboxylic acid groups help anchor the protein on the semiconductor surface, which is essential for the flow of electrons in the cell [42].

Likewise, using nanostructured materials to construct DSSC improves the energy efficiency conversion. Better yet, using doped materials is a milestone in efficiency improvement. Therefore, current trends include using materials doped with nanostructures due to their high efficiency.

Therefore, this work focuses on studying the pathway of the effects of dyes extracted from natural sources, specifically from algae, and their behavior under controlled conditions. Moreover, this work addresses the behavior of the data on the electrochemical characterization and optical absorbance of the dyes and the processing of nanometer-sized powder through mechanical grinding. This study will provide information that could lead to further research on solar cells sensitized with natural dyes as an application.

2. Materials and Methods

2.1. Synthetic and Natural Dyes

Some algae contain carotenoids, which are organic pigments found in the chloroplasts and chromoplasts of plants and other photosynthetic organisms such as certain fungi and bacteria. In plants and algae, carotenoids play an essential function by absorbing light energy for photosynthesis and protecting the chlorophyll from light damage. Their carotenoid pigments provide the characteristic red, yellow, and orange colors of many flowers and fruits and the various fragrances derived from them. Carotenoids generally absorb wavelengths between 400 and 550 nanometers (purple to green light) [19–21].

Zumahi et al. [43] studied the dye solutions obtained from various organic species using the ultrasound-assisted approach and water and ethanol as solvents. They found a predominant absorbance in the visible range from 400 nm to 700 nm and identified peaks corresponding to Phycocyanin (it is also a natural pigment that appears in blue-green algae), (618 nm); chlorophyll a and b (algae have a pigment called chlorophyll that they use to convert sunlight into food), (665 nm and 627 nm, respectively); γ and β carotene (algae contain a wide variety of pigments that give rise to the colors we see in them, such as orange), (497 nm and 478 nm, respectively); and Phycoerythrin (common pigment found in blue-green algae and red algae), (545 nm), among others. In addition, they reported an increase in the dyes' direct bandgap after 60 days from 2.05 eV to 2.32 eV and a constant refractive index ranging from 1.50 to 1.55.

2.2. Colorants' Optical Response

Algae in DSSC offer several advantages, such as being renewable and sustainable dye sources and having a lower production price than synthetic dyes. In addition, using algae in DSSC can also help to reduce carbon emissions by taking advantage of algae's ability to capture CO₂ during photosynthesis. However, research is continuing to optimize the efficiency of algae-based DSSC. Several types of algae have been previously investigated for applications in dye-sensitized solar cells (DSSC). In this sense, Table 1 shows some examples: *Chlorella vulgaris*: this microalgae species has exhibited great potential for use in DSSC due to its high chlorophyll content and stability under light exposure; *Haematococcus pluvialis*: this microalgae species contains a pigment called astaxanthin that exhibits high adsorption and stability properties, making it a suitable candidate for use in DSSC; *Dunaliella salina*: this microalgae species is a rich source of beta-carotene, which has exhibited a high absorption

coefficient in the visible light region; *Spirulina platensis* [44]: this blue–green algae species has been found to contain a pigment called Phycocyanin that has been used as a sensitizer in DSSC; cyanobacteria: cyanobacteria are also known as blue–green algae, which have been extensively studied for the use of their pigments in DSSC. The latter are some examples of algae species that have potential within the DSSC field. Nonetheless, more research is needed to optimize the efficiency of algae-based DSSC.

Table 1. Summary of microalgae species with great potential in the use of DSSC.

Algae Type/Colorant	Extraction Technique	Medium	FF (%)	Voc (V)	η (%)	Ref.
<i>Porphyridium cruentum</i>	Centrifuged, ultrafiltration, and chromatography with an anion exchange column	Acetic acid–sodium acetate buffer	0.569	0.545	1	[40]
<i>Palmaria decipiens</i>	Mortar crush, centrifuged. Phycoerythrin was purified using Sephadex G-25 disposable columns	Milli-Q water	0.67	0.53	0.12	[41]
<i>Delesseria lancifolia</i>	Mortar crush, centrifuged. Phycoerythrin was purified using Sephadex G-25 disposable columns	Milli-Q water	0.45	0.45	0.08	[41]
<i>H. pluvialis</i>	Column chromatography,	Modified WC medium	0.72	0.449 V	0.1	[45]
<i>Spirulina platensis</i> .	Ultrasonicated and centrifuged.	Water, ethanol, and acetone and pure.	-	0.75	1.2	[46]
<i>Arthrospira maxima</i>	Centrifuged	CaCl ₂	-	-	2.29%	[47]
<i>Spirulina</i> sp.	Freezing and melting technology under ultrasonic.		-	0.407	-	[48]

Moreover, water absorbs red and infrared radiation in the first few meters of its surface, and marine algae must be adapted to capture that light in addition to light with shorter wavelengths. In algae, chlorophylls, phycobiliproteins, and carotenoids capture light for photosynthesis.

Several variables have been used to characterize the optical properties of organic and inorganic colorants. For example, band gap and absorbance from optical materials are associated with potential efficiency in biosensitized solar cells (BSSC) [44]. Table 2 shows the main optical properties of some organic and inorganic materials.

Table 2. Colorant optical properties.

Colorant	Absorbance/Emission (nm)	Bandgap (eV)	References
Phycobiliprotein	490/546/576	-	[40]
Phycocyanin	400/670	-	[40]
Luteol	425/445/475	-	[40]
Clorophyle	446/670	-	[45]
Rhodamine B	532/560	2.04–2.09	[48,49]
BODIPY	485/530	1.49	[50,51]
Methyl red	410/-	2.23	[52,53]

2.3. Optical Properties Algae

Algae strongly absorbs light in the visible spectrum due to substances such as chlorophyll, carotene, betaine, or anthocyanin, among others, that are present in these organisms and provide their color. For example, green algae absorb light in the blue and red regions, corresponding to chlorophylls a and b. Therefore, they exhibit a high reflection of green light. On the other hand, brown and red algae contain carotene and anthocyanin, respectively, which determines their absorption and reflection spectrum.

The optical properties of algae have been studied by using different approaches. For example, Wangpraseurt et al. [52] used pulse amplitude modulated fluorimetry to measure chlorophyll (Chl) fluorescence in microalgae at different densities. This work focused on the photosynthesis process. The Chl fluorescence experiments were conducted using a blue LED with emissions at 460 nm. Williamson et al. [53] analyzed glacier algae in terms of ecology and their influence on ice melting by increasing solar energy absorption. One of the optical techniques used to study snow algae biomass consists of measuring the chlorophyll peak absorption at 680 nm. Structural color is another characteristic studied in algae. Lopez-Garcia et al. [54] studied the brown algae (*Cystoseira tamariscifolia*) surface. They found that the selective wavelength reflection in this species ranging from 440 nm to 550 nm depends on their photonic crystal structure, although structural color is mainly present in low illumination environments.

The optical performance of algae has also been studied through ecofriendly processes. For instance, Gu et al. [55] synthesized CuO nanoparticles using the brown alga *Cystoseira trinodis*. They conducted experiments to analyze the optical absorbance and found peaks at the UV region (226 nm and 330 nm). Moreover, photoluminescence spectra showed an emission ranging from 470 to 546 nm. Semiconductors have also been synthesized for energy applications. Sharma et al. [56] used a green approach to synthesize titanium dioxide (TiO₂) nanoparticles by using alga *Chlorella pyrenoidosa* and using graphene oxide (GO) to make a nanocomposite. UV-Vis spectroscopy showed an increase in light absorbance in the UV region, which may potentially favor efficiency in solar cells. Furthermore, the band gap was reduced from 3.14 eV in the pure TiO₂ to 2.98 eV in TiO₂-GO.

3. Results

3.1. Electrochemical Characterization of Sensitized Solar Cells Based on Natural Dyes

Due to the complex electrolyte–electrode pair redox in dye-sensitized solar cells (DSSC), the research community has adopted electrochemical techniques to fully understand the electron transfer carriers in these devices [57–59]. Photoelectrochemical reactions dictate the internal phenomena inside the DSSC, which affects the global conversion efficiency [60]. In this regard, great attention has been paid to studying the key DSSC parameters, such as electrical resistance, electron transfer, porosity change, the recombination of photoelectrons, and stability. As a note, semiconductor materials for solar cells have an absorption spectrum that is often limited to the UV region. To overcome this barrier, organic and natural dye sensitizers with high absorption in the visible region have been used [61,62]. Nevertheless, this process adds complexity to mechanism understanding, and here again, techniques such as electrochemistry or spectroscopy play a vital role [63].

3.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is the preferred method to study the mechanism behind DSSC. This technique is a powerful tool based on an alternating signal, and the results are obtained by modifying the frequency signal [64–66]. The latter is essential since this can be used to model the emerging nanomaterials' resistive, capacitive, and inductive behaviors. Furthermore, an EIS analysis can be used to estimate electrochemical and photoelectrochemical parameters such as the electron life, diffusion coefficient, and electron charge transfer resistance. To this end, equivalent circuit models have been proposed to analyze each mechanism inside the fabricated DSSC. The plotted Nyquist diagram of the EIS DSSC data set is commonly divided into three regions. Region I is the first semicircle observed at high frequencies and is related to the charge transfer resistance (R_{ct}) at the counter electrodes–electrolyte interface. Region II is assigned to the semicircle at middle frequencies and is ascribed to the recombination resistance (R_{ec}) of the TiO₂/dye interface. Finally, in region III, at low frequencies, the diffusion process of the species is presented [58,67].

Singh et al. [68] studied the Nasturtium flower dye extract as a natural photosensitizer in DSSC. They used EIS measurements with dark and open-circuit potential to elucidate

the interfacial charge of the assembled DSSC. The EIS analysis revealed that the assembled DSSC with the yellow extracted dye had the lowest Rec compared to the orange one. In other words, the yellow-tinted DSSC experienced a more significant electron recombination that resulted in the decay of the open-circuit potential. The small value of Rec in the yellow flower might have been related to the high content of carotenoids in this extract, which increased the electron density in the semiconductor and diminished its capacity to absorb light in the visible region. The latter can be explained by the lower content of functional groups that help anchor the dye to the TiO₂ surface.

As mentioned before, EIS is a powerful tool that is used to estimate most internal DSSC electrical parameters. An interesting work was developed by Fakharuddin [69], where the electron lifetime was estimated through the bode plot constructed from the EIS data and using Equation (1):

$$\tau = \frac{1}{2\pi f_{max}} \quad (1)$$

where τ is the electron lifetime (s) and f_{max} is the peak frequency maxima of the bode plot that corresponds to the charge transfer process of the anode and electrolyte. Meanwhile, the versatility of the charge storage of the nanomaterials can be determined by

$$C = \frac{\tau}{Rec} \quad (2)$$

Kaur et al. studied the bimetallic implantation of Ag-Au into the TiO₂ structure with the ion implantation technique [70]. They found that the physical treatment strongly influenced both the electron life and capacitance. For example, samples A4 and A5 were prepared by implanting Au-Ag with 9×10^{15} and 1.2×10^{16} ion cm⁻², respectively. Figure 1 displays the Nyquist and bode plots for the A4 and A5 samples. Figure 1a shows that the A5 sample had a significant charge transfer resistance (34.54 W cm²). The authors estimated the electron lifetime using Equation (1) (Figure 1b). They found that the better performance of A5 was due to its large electron lifetime, 23.90 ms. In comparison, A4 had a value of 21.83 W cm².

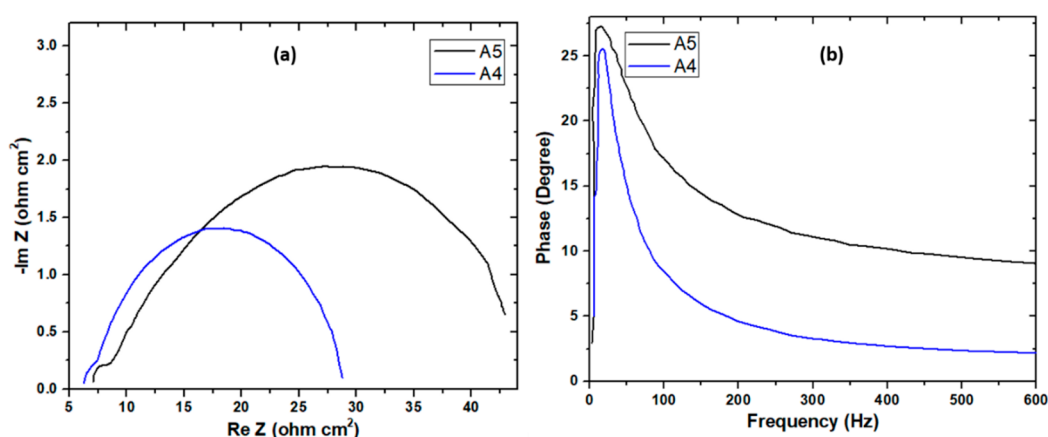


Figure 1. EIS measurements. (a) Nyquist plot. (b) Bode plot, adapted from reference [70].

Singh et al. explored why orange Nasturtium flowers considerably enhance electron lifetimes (588 μ s) compared with the yellow ones (459 μ s) [68]. The latter can be attributed to the low Rec resistance of the orange dye that retrains the recombination of electrons and iodine species.

Another interesting work was presented by Esakki et al., where natural dyes were used in ZnO-based DSSC [71]. To deeply understand the mechanism that causes the resulting abnormal behavior, they conducted an EIS test. From the voltage–current plot, a minimal current density was observed when the ZnO-based photoanode was dyed with a red Xiora extract. A regular charge recombination rate was observed from the radius of the Nyquist

plot. Moreover, the authors calculated the electron lifetime from the bode plot. Surprisingly, they found that the low efficiency of red Ixoradye in the assembled DSSC was caused by a smaller carrier lifetime. Surprisingly, algae-based DSSC were also studied by using the EIS test. For example, Lim et al. reported using chlorophyll and xanthophyll as cosensitizers in DSSC. They found that a two-fold increase in efficiency can be obtained by mixing the mentioned pigments. The authors stated that the improvement was caused by the expansion of the electron lifetime and a small electron recombination process [72].

As previously mentioned, the capacitive behavior of natural dye-based DSSC can be indirectly determined from the Nyquist and bode plot (see Equation (2)). A recent research work published by Alkali et al. illustrates the importance of conducting a capacitance analysis on DSSC [73]. This research group used three pigments extracted from *Striga hermontheca* (SH), *Bougainvillea* (BG), and *Mormordice charantia* (MC) plants. The first experiments showed very low current densities, which was attributed to the poor effect of natural dyes in modifying the adsorption spectra of the TiO₂ material in DSSC. In an attempt to improve the global electrical efficiency, the authors used cosensitization by mixing the pigments, and they used the pigments to dye the photoanode. A notorious improvement of approx. 24-fold was observed from the *J*-*V* curve. The EIS analysis revealed an increase in capacitance (0.47 mF) for the BG:SH sample, while the photoanode sensitized with MC only had a capacitance of 0.21 mF. Likewise, Faraz et al. conducted an electrochemical characterization based on EIS to gain insight into electron transport, potential, and frequency dependence [74]. The authors used the Mott–Schottky plot to determine the electrical parameters of the DSSC.

3.3. Cyclic Voltammetry

EIS is not the only technique that has been used to characterize the photoelectrochemical properties in natural dye-sensitized solar cells. It has been demonstrated that the material band gap has a great correlation with the theoretical electrochemical energy gap (EEG), which can be obtained by [75]

$$EE_G = E_{ox} - E_{red} \quad (3)$$

where E_{red} and E_{ox} are the reduction and oxidation potentials, respectively (see Equation (3)). Aderne et al. investigated the energy band gap determination of organic optoelectronic materials [76]. Figure 2 shows the cyclic voltammetry (CV) measured by this group using graphite as a working electrode and an electrolyte containing a Zn5BrTTP molecule. The CV revealed the quasireversible oxidation and reduction process, and the redox potential was calculated considering each reaction's onset potential. In this regard, two constructive lines with the same slope as the upward and downward curve were used at the redox region. One line represents the baseline current, and the other follows the slope of the fast-rising current. The intercept of these lines represents the onset potential of each reaction. For example, in Figure 2, the onset for the oxidation reactions occurs at 0.51 V while the reduction occurs at −1.46 V. Thus, the $EE_G = 0.51 - (-1.46 \text{ V}) = 1.97 \text{ eV}$.

The author explains that the data were compared with the bandgap obtained from UV–Vis measurements that were 1.86 eV, a value that is very close to the electrochemical one. The slight difference between the optical band gap and the EEG is because the former quantifies the slow adiabatic charge process that gives the material enough time to accommodate to the charge. Meanwhile, the optical band gap involves electronic transitions from the ground to the excited state due to the incident photon.

The research group of Oladipo conducted CV measurements to verify the catalytic activity of the carbon-supported Ni_{0.5}Zn_{0.5}Fe₂O₄ as a counter electrode in natural betalain dye for DSSC applications [77]. They recorded the CV to determine the efficacy of the natural dye in the DSSC performance. This research group used the CV to estimate the band gap and conducted a CV test to understand the role of the counter electrode for the iodine reduction. From the CV, the authors observed that the estimated EEG matched the UV–Vis spectrum.

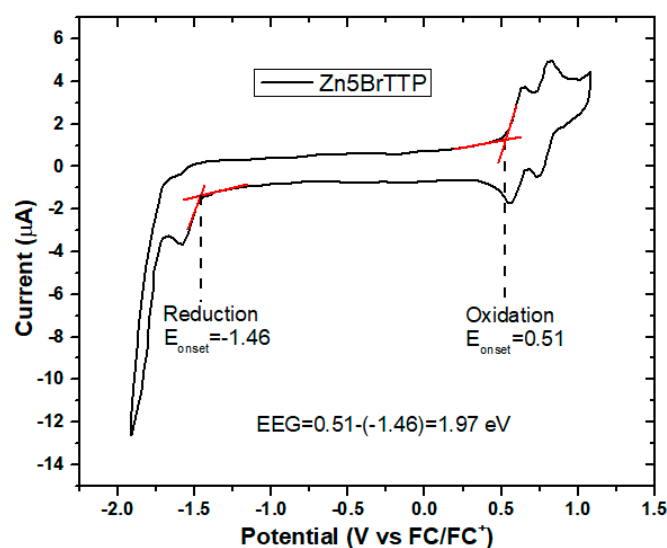


Figure 2. Voltammogram of ZnBrTTP using graphite as working electrode and Ag/AgCl counter electrode and Pt wire as a counter electrode. Information adapted from [76].

Figure 3 displays the CV for the natural dyes extracted from the leaves of *Euodia meliaefolia* (Hance), Benth, and *Corylus heterophylla* Fisch in 0.1 mol L⁻¹ KNO₃ as supporting electrolytes, as reported in [78]. As can be seen, the samples delivered different onset potentials for the pair redox reaction. Liu et al. calculated the *HOMO* and *LUMO* energies for both natural dyes. In the case of the *HOMO* energies, they proposed Equation (4):

$$HOMO = -e(E_{ox} + 4.40) \quad (4)$$

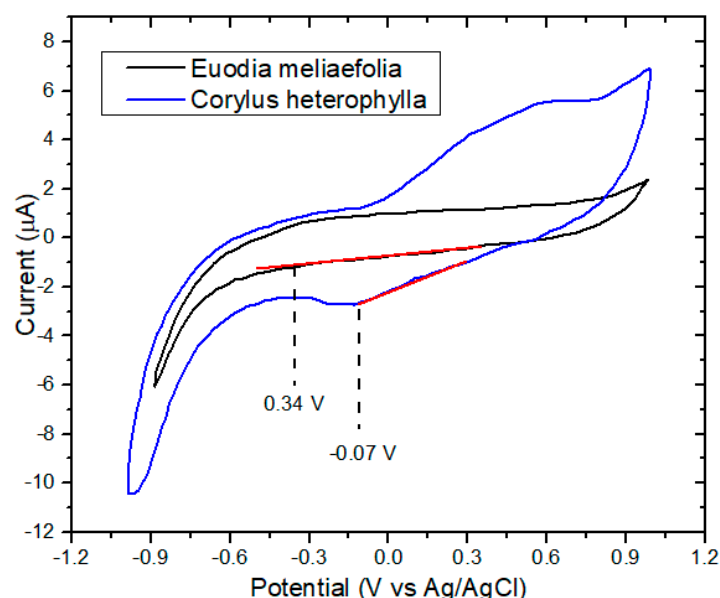


Figure 3. Voltammograms of natural dyes in 0.1 mol L⁻¹ KNO₃ at 50 mV s⁻¹ with glassy carbon as a working electrode and Pt wire as counter electrode. Adapted from [78].

In this way, the *Euodia meliaefolia* has a *HOMO* energy of −4.74 eV, while *Corylus heterophylla* has a *HOMO* energy of −4.33 eV.

The results suggest that cosensitization has an open avenue for many applications. Golshan et al. explored this approach to deploy panchromatic light-harvesting DSSC [2]. To this extent, *Malva verticillata* and *Syzygium cumini* was used to extract the natural dye. The

authors achieved CV measurements in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ by using a modified glassy carbon electrode and transferring an aliquot of the extracted dye onto the surface. The counter electrode was a Pt wire, and they used a Ag/AgCl electrode as a reference. They stated that all the natural dyes have a good redox stability. In this sense, Ossai and coworkers studied the cosensitizer effect of *Carica papaya* leaves and black cherry fruit [79]. This group replicated the methodology employed by Aderne et al. [76] to determine the HOMO and LUMO energy levels (see Figure 2). The CV analysis showed that the combined natural dyes resulted in a low electrochemical gap that ultimately enhanced the electrical efficiency of the DSSC.

4. Discussion

Concerning the application of the materials, the addition of silver nanoparticles showed an improvement in the efficiency of DCCS. As demonstrated by [32], the dye of the red protein phycoerythrin extracted from Antarctic algae improved the transport of the electrons through TiO_2 when the nanoparticles were used to help anchor the protein to the surface of the electrode. Other studies about the dyes of *Cyanophyceae*, *Chlorophyceae*, *Phaeophyceae*, and *Rhodophyceae* algae and their interaction with metallic nanoparticles have also been carried out [80]. In summary, they showed a mechanism for synthesizing nanoparticles from algae. They stated that algae hyperaccumulate heavy metal ions and can remodel them into more malleable forms [81]. Algae attributes have been used to manufacture bionanomaterials where algae extracts contain bioactive compounds such as antioxidant pigments [82].

Regarding the electrochemical characterization and spectroscopy applied to natural pigments, there have been several studies about different types of algae. Yaňuk et al. [83] used spectroscopy and electrochemistry to study the properties of two families of natural pigments, β -carboline alkaloids (β Cs) and the red protein R-phycoerythrin (R-PE), in the application of DSSC. Nevertheless, De Bon et al. [84] utilized another method to extract Phycoerythrin from red algae. The species that showed the best extraction yields were *Palmaria decipiens* and *Delesseria lancifolia*. Regarding light absorption in natural pigments, Alim et al. [33] focused on the chemical modification of dyes extracted from freshwater green algae (*Cladophora* sp.) and used them as a DSSC sensitizer. Most of the work developed on algae dyes has been carried out on green algae chlorophyll.

However, some studies [46,85] have also investigated red algae from Antarctica. The results show that efficiency is low, but the proposal for alternatives opens up research developments for the DSSC. Montagni et al. [86] developed an experiment using bacterial dyes extracted from xanthophylls of *Hymenobacter* sp. UV11, a bacterium that produces reddish colonies on agar in the Antarctic region. This dye was applied as a sensitizer in DSSC, and the results showed a very low efficiency. However, the work does suggest that polysaccharides can improve DSSC performance. The pigments extracted from various strains of marine algae are advantageous since these organisms are adapted to different light sources, salinity levels, and adverse conditions [34]. For example, tolerance to high salinity is found in marine algae, although there needs to be better pH and temperature stability. Dumas et al. [87] discovered that the stability and characteristics of natural pigments, such as those from marine algae applied in DSSC, can be further improved through bioengineering. Several research groups [88,89] used engineering strategies when working with seaweed pigments to enhance light harvesting and biomass accumulation.

On the other hand, using algae (*Spirulina platensis* and *Haematococcus pluvialis*) to modify the binding of natural dyes on the surface of the photoelectrode has been reported as an innovative yet not sufficiently discussed alternative to synthetic dyes. The main idea is to increase the number of available molecules by anchoring the algal functional groups with TiO_2 . This layer acts as a buffer that increases the concentration and protects the cell from ultraviolet rays, and an increase in efficiency was reported.

Therefore, the efforts to improve the outputs of DSSC by using natural seaweed-based dyes to determine how it works as a sensitizer and interacts with different characterizations

of the DSSC system show many areas of opportunity. In this work, the area of opportunity or alternatives with natural pigments based on marine algae that can be relatively economical and friendly to the environment is shown, which should encourage the further exploration of these organisms and their sensitizing pigments in the application of DSSC.

5. Conclusions

Recently, dyes have been receiving more attention since they are closely related to the efficiency of DSSC. The use of algae (*Spirulina platensis* and *Haematococcus pluvialis*) and the union of natural dyes modifies the surface of photoelectrodes, which increases the number of molecules available to anchor the functional groups of the algae to TiO₂. This layer increases the concentration and provides protection from ultraviolet rays, which promises an increase in efficiency.

The effect of algae on different semiconductors, usually metal oxides, showed how algal cell walls react through several mechanisms, which affects the sensitization of the DSSC by modifying the photocatalytic activity. Such changes are affected by morphology, particle size, and semiconductor type. In the case of one-dimensional structures (nanometal oxides), they have a considerable effect on algal decay compared to other nanostructures.

The study of optic properties of algae in dyes is essential due to the potential applications in solar cells, optical sensors, optoelectronics, and lasers, among others. The most studied optical variables are absorbance, transmittance, emission, the optical band gap, and the refractive index.

Author Contributions: Conceptualization, E.N.A.-M., W.P.-R. and C.A.C.-A.; methodology, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; validation, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; formal analysis, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; investigation, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; writing—original draft preparation, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; writing—review and editing, E.N.A.-M., W.P.-R., C.A.C.-A., E.R.-R. and A.C.-R.; visualization, E.N.A.-M., W.P.-R., C.A.C.-A. and A.C.-R.; supervision, E.N.A.-M.; project administration, E.N.A.-M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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