Natural Dyes Extraction, Stability and Application to Dye-Sensitized Solar Cells

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ABSTRACT: In recent years, the development of new materials has contributed markedly to improving the efficiency of dye-sensitized solar cells (DSSCs). Mesoporous semiconductors, solid electrolyte, non-conventional catalysts and synthetic dyes without ruthenium have been the focus of study. With respect to the last, lanthanides and porphyrins have presented good properties, but these elements have the same disadvantage as ruthenium-based dyes; being complicated to synthesize and very expensive. These limitations have stimulated much research in the use of natural dyes as sensitizers due to their exceptional photoelectochemical properties and low cost. Furthermore, they are regarded as renewable and environmentally friendly materials. For this reason, the application of dyes extracted from annatto seeds (*Bixa orellana*), beetroot (*beta vulgaris*) and wild bilberry (*Vaccinium meridionale Swartz*) peels was explored to fabricate DSSCs. The results show that fabricated solar cells with an N3/annatto cocktail (1:0.10) could be comparable with a device made of 100% Ruthenium synthetic dye.

KEYWORDS: Annatto, anthocyanin, beetroot, DSSCs, wild bilberry

1 INTRODUCTION

In the last decade, dye-sensitized solar cells (DSSCs) have showed great potential in different exposure conditions, direct and diffuse radiation. These devices are considered the most efficient in indoor conditions relative to other conventional cells [1–5]. Not only do DSSCs use sun diffuse radiation, but also other artificial sources such as lamps or bulbs. This characteristic is notable due to the fact that the dye absorbs in a wide range of the visible spectrum (in some cases including the infrared). Also, the active layer commonly has a high molar extinction coefficient (ε) [6,7]. In DSSCs it is very important that these parameters remain constant in time. For this reason conventional DSSCs use commercial chemically stable synthetic dyes such as ruthenium, lanthanides and porphyrins complexes [2,8,9]. The problems of high costs and unavailability of raw materials have motivated recent investigations exploring the possibility of using natural dyes as sensitizers [10–12]. Compared to their counterparts, these compounds represent renewable, cheap, easy to obtain, high extinction coefficient dyes with a variety of

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colors (absorption maximum in different wavelength of the electromagnetic spectra). For this reason these dyes have been used in DSSCs; however, because the efficiencies achieved so far are not very good [10,13], novel natural components need to be investigated.

Natural dyes are commonly extracted with polar solvents such as water, ethanol and methanol [6,14–16]. In most works, the extraction is carried out by varying the solvent, temperature and pH. With regard to the last, it has been reported that at lower pH the extraction media is more effective [17]. These organic components have been demonstrated to have high extinction coefficient as well as excellent compatibility with semiconductors such as titanium dioxide (TiO_2) and zinc oxide (ZnO) [6]. The proximity of the conduction band (CB) of these inorganic semiconductors to the LUMO (lowest unoccupied molecular orbital) of some natural dyes has allowed an effective transport of electrons within solar cells [7,18].

In this article, three different methodologies to extract dyes from annatto seeds (*Bixa orellana;* sometimes called achiote), beetroot (*Beta vulgaris*) and wild bilberry (*Vaccinium meridionale Swartz*) peels were evaluated. Acetic acid, acetone, ethanol and acidic water were chosen as extraction media. Besides their extraction efficiencies (referred to as concentration of anthocyanin *Cyanindin-3-glucoside*), the effect of

temperature was also evaluated. For one month the anthocyanin content was measured every five days. Subsequently, the stability of dyes was studied during the same period of time. The stability study was realized in two environments; outdoors and by an accelerated test in a UV chamber. Finally, DSSCs were fabricated using the best dye with the highest concentration of anthocyanins and the greatest stability.

2 EXPERIMENTAL

2.1 Dyes Extraction

Initially beetroot and wild bilberry peels were rinsed with deionized water. Annatto seeds were cleaned by removing only small impurities and leaves. Subsequently, beetroot and wild bilberry peels were cut into small pieces of 1cm x 1cm. Annatto seeds were not modified. The samples were introduced in three extraction media at two different temperatures (room temperature and 37°C). Ethanol (Aldrich, 99.50%), Acetone (J.T. Baker, 99.50%), Acetic acid (Aldrich, Glacial) and water (Milipure, deionized) were used as solvents. The proposed media were chosen based on results reported in the literature [12,17], but to the best

of our knowledge these vegetal materials have not ever been studied in these media. Table 1 summarizes the composition of these media and the conditions in which the collection of the dyes were studied. The extraction media were obtained by mixing solvents for 20 minutes at room temperature in a volumetric flask. Acidic water was considered as 0.10 M HCl solution (Aldrich, 37%). Finally the volumetric flasks with their samples were placed in a bain-marie with a condenser at room temperature and 35°C.

In order to evaluate the proposed methodology, the absorbance at 510 nm and 700 nm at two different pH values (using buffers) was chosen as response variable. It was necessary to determine the total anthocyanin content (TAC) by the pH differential method [15]: $TAC_{(mg/L)} = (A * Mw * Df * 100) / (e * L)$. Where $A = (A_{510} - A_{700})_{pH\ 1.00} - (A_{510} - A_{700})_{pH\ 4.50}$, Mw is the molecular weight (g/mol), ε is the molar extinction coefficient (L/(mol cm)), Df is the dilution factor, and L is the cell path length (cm). Calculations were made with respect to anthocyanin *Cyanindin-3-glucoside* (Mw: 449.20, e: 26900). Absorbance measurements were realized in a Cary 100 UV-Vis spectrophotometer (Varian) after the dyes were filtered three times. Anthocyanin content was followed by a month taking samples every five days.

Table 1 Extraction methodologies for the proposed natural dyes.

Sample	Dye	Extraction media*	Temperature
S1	Beetroot	Acetic Acid / Acidic water	Room temperature
S2	Wild bilberry		
S3	Annatto		
S4	Beetroot		37°C
S5	Wild bilberry		
S6	Annatto		
S7	Beetroot	Acetone / Acidic water	Room temperature
S8	Wild bilberry		
S9	Annatto		
S10	Beetroot		37°C
S11	Wild bilberry		
S12	Annatto		
S13	Beetroot	Ethanol / Acidic water	Room temperature
S14	Wild bilberry		
S15	Annatto		
S16	Beetroot		37°C
S14	Wild bilberry		
S18	Annatto		

*Relation 50%v/v.

2.2 Stability Study of Dyes

The stability study was focused on dyes extracted from media that showed major TAC or better performance (one dye for each extraction media). In these, TAC was determined during a month at two conditions. In the first, dyes were exposed at ultraviolet radiation (0.89 W/m^2 * nm, 60°C) in a UV chamber QUV (Q-Lab). With relation to the outdoors test, global radiation and temperature records were taken to know the dose values of these variables on the dyes. Data were collected from a Vantage Pro weather station (Davis Instruments) (4 data per hour).

Given that the dyes could be oxidized over time, two commercial antioxidants were also mixed with the dyes and analyzed, Irganox® (A1) and Irgafos® (A2) (Ciba, BASF); and evaluated at 1.00x10^{-3} %p/v.

2.3 Cyclic Voltammetry

The LUMO and HOMO of dyes without antioxidants were estimated by cyclic voltammetry (CV). The measurements were made by a Potentiostat-Galvanostat (Autolab) using an electrochemical cell with a graphite electrode, platinum wire (counter), 0.20 M Sodium Acetate (Buffer, pH 4.50) (supporting electrolyte), Ag/AgCl (KCl$_{satured}$) electrode (reference electrode), and nitrogen gas to prevent premature oxidation of samples during the test.

2.4 Fabrication of Solar Cells

Four cells were fabricated and evaluated by standard procedures reported elsewhere [19]. To fabricate the mesoporous layer, ZnO nanoparticles (Aldrich) were used. The average size of these was 100 nm. The crystalline powders of ZnO had a wurtzite content of over 80%, with specific surface area of roughly 11 m^2/g. The ZnO powder was dispersed in a mixed solvent of terpineol (Aldrich, ~95%) and ethanol (Aldrich, ~99.5%) containing ethyl cellulose (Alfa Aesar) as a binder. The resulting viscous paste was coated on an F-doped SnO$_2$-coated glass (Solaronix, TCO30-8) as a transparent conductive oxide substrate using a screen-printing technique. The coated substrates were sintered in sequence at 330°C for 5 min, 380°C for 10 min, 450°C for 15 min, and 500°C for 15 min, resulting in a porous semiconductor ZnO electrode.

Ruthenium complex dye N3 (Cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)) (Solaronix, Ruthenizer 535) was used as the control photosensitizer. This dye and cocktails were prepared in a mixed solvent of acetonitrile and tert-butyl alcohol (50:50 v/v). The concentration of the used solution of N3 was 0.3 mM. Table 2 shows the studied ratio in the proposed cocktails. For the dye adsorption, the porous semiconductor electrodes were heated to 450°C for 30 min to clean the semiconductor surface just prior to immersing them in the dye solution. The process was carried out at room temperature for 2 h and 20 h, after which the electrode was rinsed with acetonitrile.

The counter electrode was prepared by casting a platinum precursor (Solaronix, Plastisol T) onto an FTO-glass substrate followed by sintering at 450°C for 30 min. The electrolyte composition was 0.03 M I$_2$ (Aldrich), 0.6 M 1-methyl-3-butylimidazolium iodide (Aldrich), and 0.1 M guanidinium thiocyanate (Aldrich) in acetonitrile/valeronitrile (85:15). The photoelectrodes and the counter electrodes were arranged in a face-to-face cell layout and then filled with the electrolyte. Figure 1 shows the proposed design of the fabricated solar cells.

Table 2 Dye concentrations used in the fabricated solar cells.

Solar cell	Synthetic dye*: Natural dye**
C1	1: 0
C2	1: 0.10
C3	1: 0.20
C4	0: 1

*N3 dye (*cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II)*): 3.00x10^{-4} M in a solution of Acetonitrile and Tert-butyl alcohol (volume ratio 1:1) [33,34].
**Acidic solution (14%v/v).
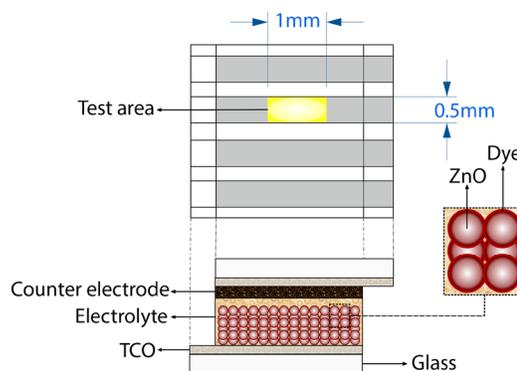
Figure 1 Scheme of the fabricated solar cells. Effective area of photon conversion: 0.50cm^2.

3 RESULTS AND DISCUSSIONS

3.1 Extraction

Acetic Acid/Acidic Water

Figure 2 shows the results obtained for each source in the extraction media acetic acid/acidic water. The data clearly demonstrate the effect of temperature on TAC values during the period studied. The diffusion of anthocyanin over time is very visible from peels and seeds to extraction media. At 37°C, TAC values in each media were higher with respect to room temperature (except S5 at 15 and 30 days). At 30 days and 37°C, S4 and S6 reached maximum values of 14.20 g/mL and 22.40 g/mL respectively. This was expected due to the effect of temperature on the dissolution of anthocyanins in the extraction media [20]. Increasing the extraction efficiency is remarkable; however it is very important to mention that at higher temperatures (above 50°C) the anthocyanins and other phenols could suffer irreversible changes that would affect their absorption range.

In general, it can be concluded that during the studied period of time, all media presented an increasing TAC; S5 probably suffered a premature oxidation between 25 and 30 days. This media can presumably be more stable due to the presence of acetic acid, which is considered as a preservative.

Acetone/Acidic Water

The results of TAC in extraction media acetone/acidic water are summarized in Figure 3. Once again the extraction media with wild bilberry (S8) presented a tendency to oxidize from day 20. Both room temperatures (S8) and 37°C (S11) presented this problem.
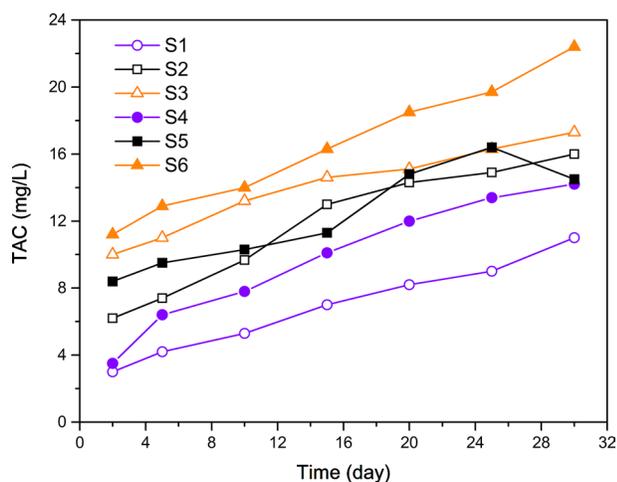
The results show that dyes extracted from wild bilberry peels probably have higher antioxidant content compared with dyes from beetroot peels and annatto seeds. It is well known that compounds that are easier to oxidize are often the best antioxidants (molecules which can donate a free electron or hydrogen atoms to reactive free radicals). This result agrees with that reported by Garzón [21]. On the other hand, it has been found that the antioxidant activity of berries is directly proportional to the TAC [22]. For annatto and beetroot this relation has not been found due to interaction of its anthocyanins with other important molecules such as bixin and betanine [23,24].

The premature oxidation of S8 and S11 compared to S2 and S5 can be related to formation of more unstable chemical intermediates [25] with anthocyanins (isolated molecules with little interaction) due the lower polarity of acetone compared to acetic acid [26].

Figure 3 also shows that the extraction media with annatto seeds (S12) reached higher TAC value compared to other sources at 30 days (S9: 16.30 mg/L, S12: 21.90 mg/L). On the other hand, TAC values obtained for S7 and S10 were very similar at the same period, 11.90 mg/L and 11.20 mg/L respectively.

Ethanol/Acidic Water

Figure 4 clearly ratifies the annatto seeds as the main source of anthocyanins (S15: 18.50 mg/L, S18: 19.50 mg/L at 30 days). Once again the extraction media for wild bilberry (at room temperature and 37°C) presented a tendency to oxidize after day 15. Oxidation related to the latter media (acetone/acidic water) was more rapid, probably due to differences in the dipolar moment between ethanol (1.69D) and acetone

Figure 2 TAC values in acetic acid/acidic water extraction media. Black-filled symbols represent extraction at 37°C. Unfilled symbols at RT.
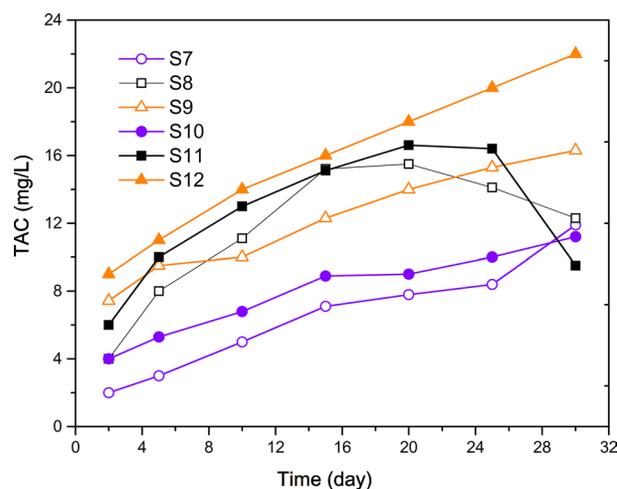
Figure 3 TAC values in acetone/acidic water extraction media. Black-filled symbols represent extraction at 37°C. Unfilled symbols at RT.

(2.91D), decreasing the formation of stable chemical intermediates with the anthocyanins due to poor formation of hydrogen bonds. In general, ethanol/acidic water media presented both lower TAC values and an unstable extraction system for all the vegetal sources. Probably, this result can be attributed to the high vapor pressure of ethanol coupled with the exposure time and temperature proposed.

Regarding the mentioned above, for the studied dyes the most critical selection factors of the tested extraction media were the polarity index and chemical stability (vapor pressure) of the organic solvent mixed with the acidic water. For this reason, the acid acetic/

Figure 4 TAC values in ethanol/acidic water extraction media. Black-filled symbols represent extraction at 37°C. Unfilled symbols at RT.

acidic water solution was the most promising extraction media.

3.2 Stability Study

A stability study was realized for the dyes extracted from methodologies S6 (25 days), S4 and S5 (30 days). New dyes were extracted following the procedures mentioned above to accomplish this part of the study.

Outdoors Exposition
Table 3 shows the radiation and temperature conditions to which the dyes were exposed. The average data are cumulative for each of the days evaluated. Clearly, average values calculated show normal variations common to tropical climate in the summer season.

In Figure 5 it can be seen that A2 antioxidant presented a better behavior than A1, probably due to its good solubility in the media studied compared to A1.

After 30 days of exposition, TAC values for annatto decreased up to 50%. Although this is a considerable loss, dyes under normal conditions of exposition within solar cells can be more stable due to their electrochemical regeneration (function of electrolyte) and lower oxygen concentration (encapsulating of solar cell in an inert atmosphere).

UV Chamber Exposition
The results of TAC at UV radiation are summarized in Figure 6; A1 and A2 antioxidant did not contribute

Table 3 Average radiation and temperature data in the exposition period outdoors.

Day	Temperature* (°C)		Radiation* (W/m²)	
	Mean	Standard deviation (σ)	Mean	Standard deviation (σ)
0	---	---	---	---
2	24.45	2.30	245.23	30.22
5	23.22	1.42	243.32	20.20
10	23.25	2.02	207.40	23.30
15	22.02	3.16	202.13	23.01
20	19.01	4.32	210.73	30.24
25	20.22	2.34	211.24	23.20
30	24.83	4.04	285.35	27.03
	**Tm: 22.43		**Rm: 229.34	

*Average / 24 hours (day)
**Average at 30 days
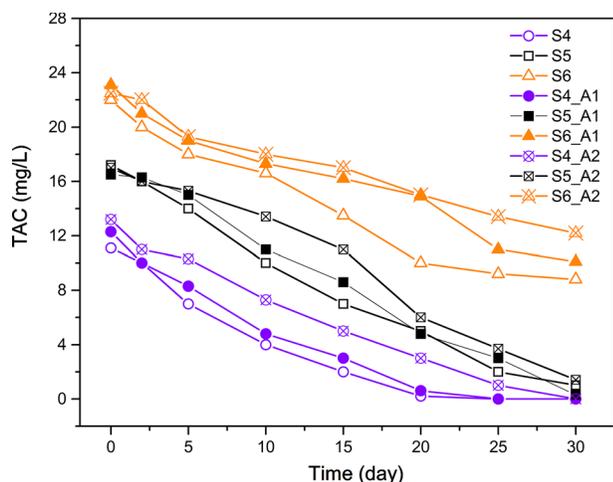
Figure 5 TAC values for the studied dyes at outdoors exposition.
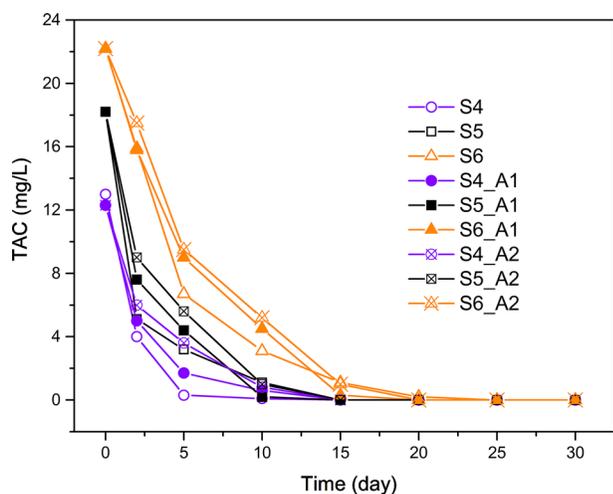
Figure 6 TAC values obtained during UV chamber exposition.

to the stabilization of TAC. These data were expected due to very extreme conditions within the chamber that generated premature oxidation of dyes. The exposition temperature was high (60°C) and produced an inevitable loss of anthocyanins [16,27]. Once again, it is very important to understand how the stability of annatto media stands out with respect to other sources.

Correlation between Outdoors and UV Chamber
The obtained correlation was made only with annatto dye due to its high stability during evaluation time.

Figure 7 shows the correlation obtained with the exposure media, taking into account variables such as temperature, radiation and time. This applies only
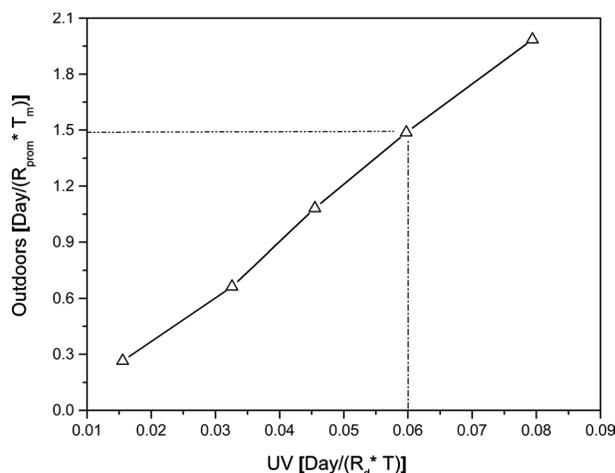
Figure 7 Correlation between UV Chamber and Outdoors measurements, considering radiation and temperature in each exposition media. Curve applies only between 1–4 days at UV Chamber (R2: 0.9970). UV Chamber (Rd = 0.89 W/m²*nm, T = 60°C – Outdoors (Rprom = Rmª / 340nm, Tmª). ªData taken from Table 3.

between 1–4 days under UV chamber exposition. After 4 days, dyes were degraded in this exposure media. For example, UV factor equals 0.06 corresponds to Outdoors factor value of 1.49. According to this, 3.19 days in an UV chamber will be equivalent to 22.46 days outdoors. This correlation is a first approach to develop a model that allows relating laboratory measurements (simulated media) with real data for these particular dyes and particular weather conditions.

3.3 Cyclic Voltammetry

Figure 8 presents the obtained voltammograms for the extracted dyes. Beetroot has lower oxidation potential (E_{ox},0.72 V) than other dyes, probably due to its antioxidant activity. Wild bilberry and Annatto have values of 0.77 V and 0.81 V respectively. Once again, annatto dye is also promising from this point of view. The estimated LUMO and HOMO obtained for the dyes are summarized in Table 4.

Figure 9 shows a comparison between energetic levels of natural dyes obtained, ruthenium dye (N3) and semiconductors commonly used in DSSCs (TiO$_2$ and ZnO). For the natural dyes, band gap was calculated from onset in the UV-Vis spectra shown in Figure 10.

These energetic diagrams are very useful in predicting the solar cell behavior. The difference between the energetic levels of the dye (LUMO) and semiconductor (quasi Fermi level) should be near to 1 eV in order to contribute to improving the electron injection rate in the CB of the semiconductor [28]. Its difference is commonly called electron injection overpotential (EIS).
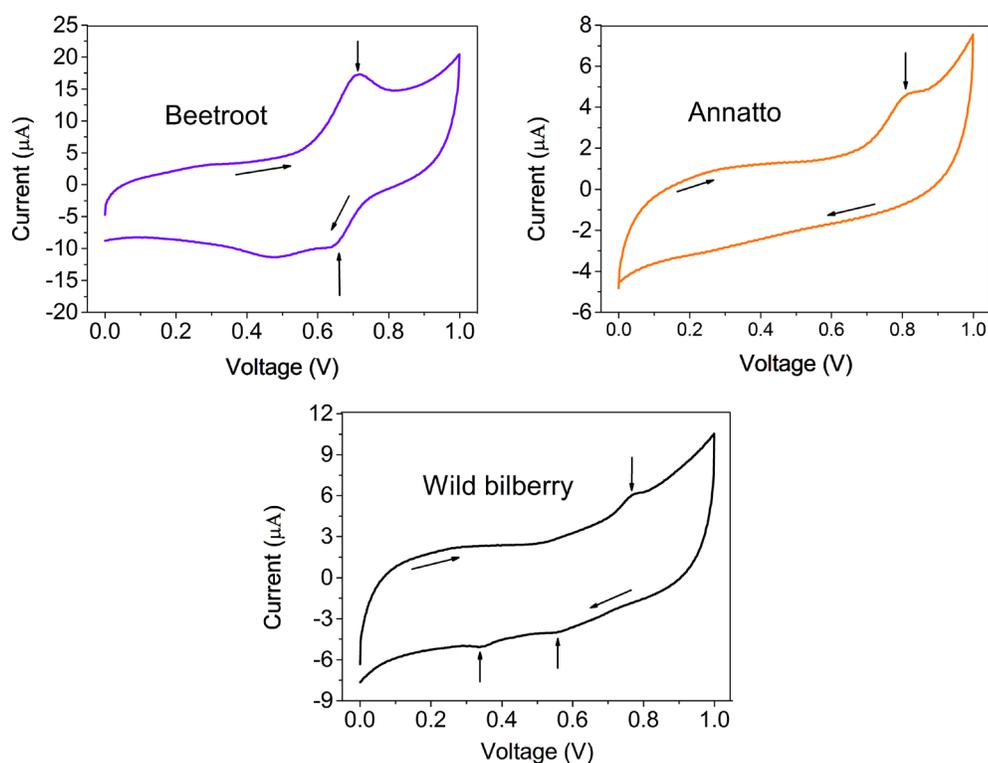
Figure 8 CV curves for the studied dyes at positive potential (1V/s). These electrochemical measures were referred to as Ag/AgCl, KCl$_{satured}$ electrode. Vertical arrows denote first oxidation couples.

Table 4 Calculated values of HOMO, LUMO and optical band gap determined in each extracted dye.

Dye	HOMO[1] (eV)	LUMO[2] (eV)	Eg[3] (eV)
Wild bilberry	− 5.07	− 1.81	3.26
Beetroot	− 5.08	− 3.11	1.97
Annatto	− 5.21	− 2.85	2.36

[1]Homo (eV) = −(4.40 + E$_{ox}$)[35]
[2]LUMO estimated from HOMO-LUMO = Eg
[3]Calculated band gap from onset in the UV-Vis spectra: Eg (eV) = 1240 / λ(nm).

Figure 9 clearly shows that the EIS value for beetroot and annatto dye is suitable to build DSSCs and is similar to N3. Wild bilberry dye will have limitations due to the wide energy gap with both semiconductors. On the other hand, the difference between HOMO of the dye and the redox potential of the I$_3^-$/I$^-$ reaction of the electrolyte is called dye regeneration overpotential (DRO), and it should be close to 0.6 eV in order to avoid undesirable reactions within the electrolyte. It can increase the recombination rate of electrons in the interface dye/electrolyte. It is important to note that DRO values are below 0.6 eV for all dyes shown in Figure 10, but it is not a limiting factor because it has been shown that iodine electrolytes have slow recombination kinetics. Some people prefer to use other kinds of materials such as Spiro-OMeTAD or P3HT to avoid this problem. This is the case of the solid-state dye-sensitized solar cells (ss-DSSCs) [29].

3.4　I-V Measures

Based on the extraction results, stability, and cyclic voltammetry presented in this report, annatto dye was chosen to be part of the solar cells design. During the course of these studies, annatto dye has always shown the highest performance compared to the other extracted dyes.

Figure 11 presents the results of the efficiency obtained for the fabricated cells using as a reference synthetic dye N3 (C1) from parameters obtained from Figure 12. Clearly, efficiency falls when the natural dyes were included as active layers, but it is important to note that within the standard deviation of the results some values for C1 and C2 are coincidental, showing a positive response when mixing annatto dye with the synthetic reference. With respect to C3 and C4, the efficiency value
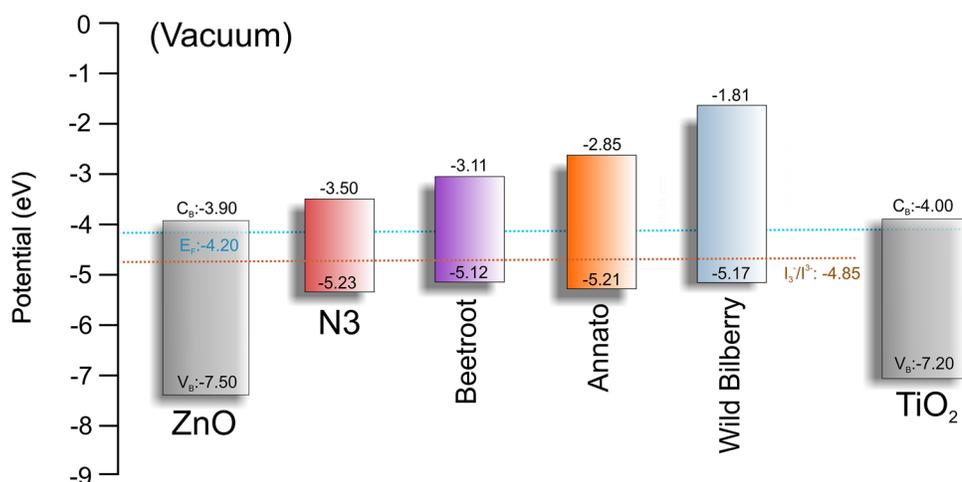
Figure 9 Relation between energetic levels of the studied dyes and conventional semiconductors used in a DSSC architecture.
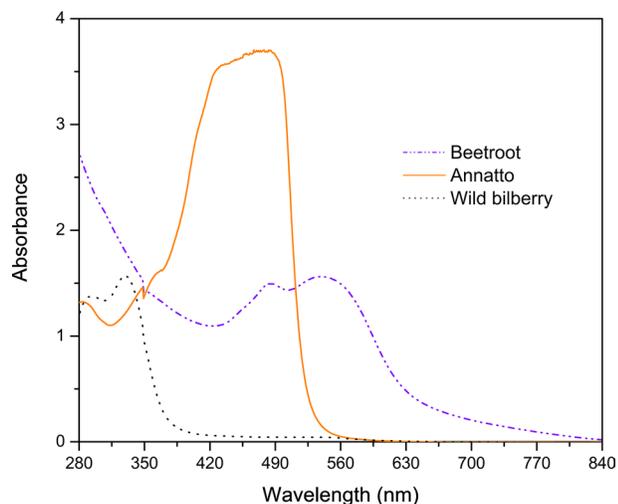
Figure 10 UV-Vis absorption spectra of the extracted dyes.
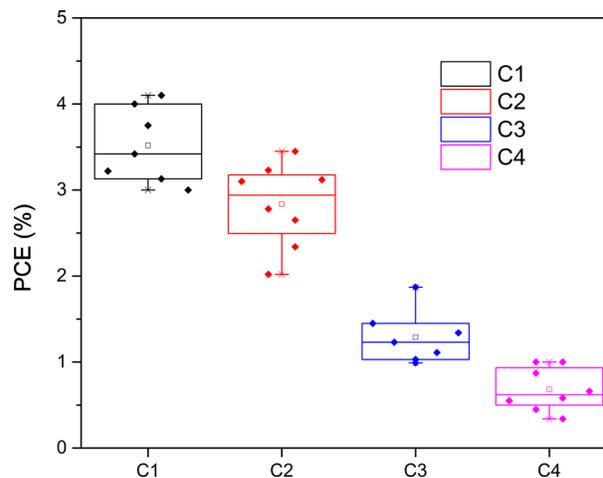
Figure 11 Efficiency of fabricated DSSCs with the obtained natural dyes.

is lower, but the latter is much better than the reported values for some natural sources mentioned in the literature [10,24]. Additionally, the obtained efficiency values for C4 are better than solar devices made with blueberry dye [13], which present low stability due to the fact that it is principally comprised of highly-antioxidant anthocyanins such as cyanidins (Cn) and delphinidins (Dp) [22,30]. Overall, results are very promising since we can consider that the cells manufactured give us a great view of the behavior and potential use of natural sources as partial substituents of synthetic compounds. This could represent a decrease in production costs and energy payback time (EPBT) and have a long-term positive impact on the environment.

In the evaluation of solar cells, it is very appropriate to show some parameters which are used to calculate the efficiency of these devices; short circuit current (Isc), open circuit voltage (Voc) and fill factor (FF) are the variables most important to consider. The Isc and Voc values are the voltage and current maximum that solar cell can deliver. The FF is considered as the ratio of generated (Isc x Voc) and incident power on the cell. Table 5 summarizes the data obtained for cells. It shows fabricated cells to have very similar values of FF (about 60%). With relation to C2 and C3, FF was improved relative to C1 when the natural dye was added. This result is very important since natural dye contributes to capturing more of the photons. This result demonstrates the co-sensitization effect with the combination of natural and synthetic dye. It is essential to mention that the co-sensibilization with natural dyes has been little studied. Few articles have
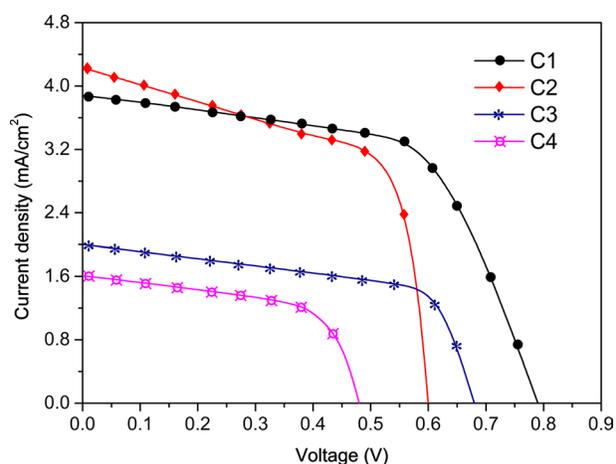
Figure 12 I-V curves for the fabricated solar devices. Rate scan: 0.05V/s.

Table 5 Data of short circuit current (Isc), open circuit voltage (Voc), and fill factor (FF) of I-V curves showed in Figure 12.

Cell	Isc (mA/cm²)	Voc (V)	FF (%)	η (%)
C1	3.88	0.79	60.3	4.10
C2	4.23	0.60	61.1	3.45
C3	2.03	0.68	60.8	1.87
C4	1.12	0.53	57.8	1.00

been published in the last decade [18,31]. For this reason, obtained results are very important to denote a new family of DSSCs, natural dye co-sensitized solar cells.

On the other hand, the Isc value of C2 is higher than that obtained for C1. This demonstrates that by replacing 10% of the synthetic dye, maxima current can be increased upto 4.23 mA/cm². With relation to C3 (20% of natural dye), Voc improved with respect to C2. This result probably is related to the variation of the chemical capacitance of constituents when solar cell suffered an increase in temperature due to repetitive large illumination periods, as reported by Raga and coworkers [32].

4   CONCLUSIONS

Acetic acid/acidic water media showed a higher concentration of anthocyanins for each of the sources (wild bilberry, beetroot and annatto) under the conditions studied. This was mainly due to its more marked polar character than the other solvents, which, in addition to its low vapor pressure, could help the environment to be more stable during the evaluation period. In this extraction media, annato dye presented the higher anthocyanins content compared with all other methodologies studied (S6: 22.41 g/mL). Temperature was an important variable in obtaining this result due to dissolution of anthocyanins that promote its migration from seeds to extraction media. This media is more stable due to the presence of acetic acid, which is considered as a preservative.

The TAC results from beetroot peels in each tested media showed a low contribution of anthocyanins during extraction time, but it is important to note that they always had a tendency to increase, unlike wild bilberry, which presented stability problems after 20 days (acetone/acidic water) and 15 days (ethanol/acidic water) in both temperature conditions.

Stability studies outdoors and in a UV chamber (accelerated test) showed that the dyes mixed with the antioxidant A2 had a better behavior. It is very important to mention that this compound presented good solubility at room temperature with wild bilberry, beetroot and annatto extracts.

The cyclic voltammetry for each of the obtained dyes showed that beetroot and annatto dye could interact efficiently with titanium dioxide (TiO_2) and zinc oxide (ZnO). Their conduction bands are very close to the LUMO of the dyes, facilitating transfer of electrons and lowering the probability of recombination.

The fabricated solar cells showed that the use of an N3/annatto cocktail presented the best co-sensitization effect and could be comparable with a solar cell with 100% of the N3 synthetic dye. This result is very important because of the likely reduction in long-term costs on the industrial level by decreasing the concentration of synthetic dye, which can cost 1000 times more than natural dye.

Finally, it is important to mention that this work provided a significant improvement in the implementation of natural dyes in DSSCs. To our knowledge, this is the first work of its kind of solar devices taking into account the following aspects: a) determination of the optic band gap, HOMO and LUMO of natural dyes; b) construction of an energy diagram correlating the obtained natural dyes with the other component materials of the device; c) the use of a synthetic/natural dye cocktail; and d) evidence of a co-sensitization effect in a synthetic/natural dye cocktail. These features highlight the potential of the use of natural dyes to reach an industrially feasible and environmentally friendly photovoltaic technology.

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REFERENCES

1. S.-Y. D. Fan-Tai Kong and K. Wang, Review of recent progress in dye-sensitized solar cells, *Adv. Optoelectron.* **2007**, 1–13 (2007).
2. H. Lin, X. Li, Y. Liu and J. Li, Progresses in dye-sensitized solar cells, *Mater. Sci. Eng. B* **161**, 2–7 (2009).
3. Y. Ogomi, S. Sakaguchi, T. Katoh, T. Kado, Y. Yamaguchi, M. Kono and S. Hayase, Dye Sensitized Solar Cells with High Photo-Energy Conversion-Controll of Nano-Particle Surfaces, *Photovoltaic Energy Conversion, Conference Record of the 2006 IEEE 4th World Conference on*, Volume **1**, pp. 167–170 (2006).
4. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, Dye-sensitized solar cells, *Chem. Rev.* **110**, 6595–6663 (2010).
5. M. Gratzel, Photoelectrochemical cells, *Nature* **414**, 338–344 (2001).
6. H. Zhou, L. Wu, Y. Gao, and T. Ma, Dye-sensitized solar cell using 20 natural dyes as sensitizers, *J. Photochem. Photobiol. A Chem.* **219**, 188–194 (2011).
7. M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol. C Photochem. Rev.* **4**, 145–153 (2003).
8. T. Bessho, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau and M. Grätzel, Highly efficient mesoscopic dye-sensitized solar cells based on donor–acceptor-substituted porphyrins, *Angew. Chem.* **122**, 6796–6799 (2010).
9. J. H. Oh, Song, Y. K. Eom, J. H. Ryu, M. J. Ju, & H. K. Kim, Wavelength conversion lanthanide(III)-cored complex for highly efficient dye-sensitized solar cells, *Bull. Korean. Chem. Soc.* **32**, 2743–2750 (2011).
10. H. Zhou, L. Wu, Y. Gao and T. Ma, Dye-sensitized solar cells using 20 natural dyes as sensitizers, *J. Photochem. Photobiol. A Chem.* **219**, 188 (2011).
11. S. Hao, J. Wu, Y. Huang and J. Lin, Natural dyes as photosensitizers for dye-sensitized solar cell, *Sol. Energ* **80**, 209–214 (2006).
12. K. Wongcharee, V. Meeyoo and S. Chavadej, Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers, *Sol. Energ. Mat. Sol. C.* **91**, 566–571 (2007).
13. H. Hug, M. Bader, P. Mair and T. Glatzel, Biophotovoltaics: Natural pigments in dye-sensitized solar cells, *Appl. Energy.* **115**, 216–225 (2014).
14. A. Castañeda-Ovando, M. d. L. Pacheco-Hernández, M. E. Páez-Hernández, J. A. Rodríguez and C. A. Galán-Vidal, Chemical studies of anthocyanins: A review, *Food Chem.* **113**, 859–871 (2009).
15. Z. Yang and W. Zhai, Optimization of microwave-assisted extraction of anthocyanins from purple corn (Zea mays L.) cob and identification with HPLC–MS, . *Innov. Food Sci. Emerg. Technol.* **11**, 470–476 (2010).
16. V. Sivakumar, J. Vijaeeswarri and J. L. Anna, Effective natural dye extraction from different plant materials using ultrasound, *Ind. Crops Prod.* **33**, 116–122 (2011).
17. G. Patil, M. C. Madhusudhan, B. Ravindra Babu and K. S. M. S. Raghavarao, Extraction, dealcoholization and concentration of anthocyanin from red radish, *Chem. Eng. Process.* **48**, 364–369 (2009).
18. C.-M. Lan, H.-P. Wu, T.-Y. Pan, C.-W. Chang, W.-S. Chao, C.-T. Chen, C.-L. Wang, C.-Y. Lin and E. W.-G. Diau, Enhanced photovoltaic performance with co-sensitization of porphyrin and an organic dye in dye-sensitized solar cells, *Energ. Environ. Sci.* **5**, 6460–6464 (2012).
19. N. Sakai, T. Miyasaka and T. N. Murakami, Efficiency enhancement of zno-based dye-sensitized solar cells by low-temperature TiCl4 treatment and dye optimization, *J. Phys. Chem. C* **117**, 10949–10956 (2013).
20. M. E. Cuevas, A. Antezana and P. Winterhalter Análisis y Caracterización de Antocianinas en Diferentes Variedades de Maíz (zea mays) Boliviano, *Memorias red-alfa Lagrotech - Comunidad europea* **2008**, pp. 79–85 (2008).
21. G. A. Garzón, C. E. Narváez, K. M. Riedl and S. J. Schwartz, Chemical composition, anthocyanins, non-anthocyanin phenolics and antioxidant activity of wild bilberry (Vaccinium meridionale Swartz) from Colombia, *Food Chem.* **122**, 980–986 (2010).
22. I. M. Heinonen, A. S. Meyer and E. N. Frankel, Antioxidant activity of berry phenolics on human low-density lipoprotein and liposome oxidation, *J. Agric. Food Chem.* **46**, 4107–4112 (1998).
23. N. López, E. Puértolas, S. Condón, J. Raso and I. Alvarez, Enhancement of the extraction of betanine from red beetroot by pulsed electric fields, *J. Food Eng.* **90**, 60–66 (2009).
24. N. M. Gómez-Ortíz, I. A. Vázquez-Maldonado, A. R. Pérez-Espadas, G. J. Mena-Rejón, J. A. Azamar-Barrios and G. Oskam, Dye-sensitized solar cells with natural dyes extracted from achiote seeds, *Sol. Energ. Mater. Sol. C.* **94**, 40–44 (2010).
25. M. C. Moncada, S. Moura, M. J. Melo, A. Roque, C. Lodeiro and F. Pina, Complexation of aluminum(III) by anthocyanins and synthetic flavylium salts: A source for blue and purple color, *Inorganica Chim. Acta* **356**, 51–61 (2003).
26. Y. Marcus, *The properties of Solvents*, pp. 142–150, Wiley Series in Solution Chemistry (1998).
27. M. A. Green, Recent Developments and Future Prospects for Third Generation and Other Advanced Cells. *Photovoltaic Energy Conversion, Conference Record of the 2006 IEEE 4th World Conference on*, Volume **1,** pp. 15–19 (2006)
28. S. Murai, S. Mikoshiba, H. Sumino, T. Kato and S. Hayase, Quasi-solid dye sensitised solar cells filled with phase-separated chemically cross-linked ionic gels, *Chem. Comm.* **13**, 1534–1535 (2003).

29. D. Beljonne, J. Cornil, C. Risko and J.-L. Brédas, Small Optical Gap Molecules and Polymers: Using Theory to Design More Efficient Materials for Organic Photovoltaics, *Multiscale Modelling of Organic and Hybrid Photovoltaics*, Topics in Current Chemistry, pp. 1–38, Springer Berlin, Heidelberg (2014).

30. M. P. Kähkönen, J. Heinämäki, V. Ollilainen and M. Heinonen, Berry anthocyanins: isolation, identification and antioxidant activities, *J. Sci. Food Agric.* **83**, 1403–1411 (2003).

31. M. Kimura, H. Nomoto, N. Masaki and S. Mori, Dye molecules for simple co-sensitization process: fabrication of mixed-dye-sensitized solar cells, *Angew. Chem. Int. Ed.* **51**, 4371–4374 (2012).

32. S. R. Raga and F. Fabregat-Santiago, Temperature effects in dye-sensitized solar cells, *Phys. Chem. Chem. Phys.* **15**, 2328–2336 (2013).

33. M. K. Nazeeruddin, E. Muller, R. Humphry-Baker, N. Vlachopoulos and M. Gratzel, Redox regulation in ruthenium(II) polypyridyl complexes and their application in solar energy conversion, *J. Chem. Soc., Dalton Trans.* **23**, 4571–4578 (1997).

34. A. Stanley, B. Verity and D. Matthews, Minimizing the dark current at the dye-sensitized TiO_2 electrode, *Sol. Energy Mater. Sol. C.* **52**, 141–154 (1998).

35. T.-A. Chen, X. Wu and R. D. Rieke, Regiocontrolled synthesis of poly(3-alkylthiophenes) mediated by Rieke Zinc: Their characterization and solid-state properties, *J. Am. Chem. Soc.* **117**, 233–244 (1995).