

Thermally and UV Stable Natural Dyes with Potential Use in Efficient Photoelectrochemical Devices

Mario Alejandro Mejía Escobar* and Franklin Jaramillo*

Centro de Investigación, Innovación y Desarrollo de Materiales – CIDEMAT, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

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ABSTRACT: Energy alternatives have been one of the most important research focal areas of the last decade due to the imminent lack of fossil fuels. This motivation has allowed the evolution of the materials science field in areas such as electrochemistry, where high availability, low cost and negligible environmental impact are the desired principal qualities. For this reason, as an example of a photoelectrochemical device, we have proposed the use of natural dyes from 37 agro-industrial wastes in dye-sensitized solar cells. We obtained dyes from red cabbage, radish and roselle wastes with a good stability for eight hours with a constant dose of UV radiation at 60 °C. In these, a strong copigmentation effect was observed at 90 °C in a few hours. Besides which, an increase in the absorption spectra close to 200% was reached with the media extraction proposed. Additionally, the fabricated solar devices reached efficiencies between 0.5% and 1.7%.

KEYWORDS: Natural dyes, agro-industrial wastes, anthocyanin content, copigmentation, photoelectrochemistry

1 INTRODUCTION

In the last decade, alternative energy sources have been the focal point of studies due to the lack of fossil fuels and the generation of high pollution. Wind, earth, water and sun have been the more studied available energy sources. With respect to the last, photoelectrochemical devices such as dye-sensitized solar cells (DSSCs) and hydrogen-producing photoelectrochemical cells (HPPEC) are considered to be attractive due to their future potential in applications related to building [1,2] and transportation [3–5]. In the case of DSSCs, special materials have allowed the absorbance of a considerable amount of photons from different sources and remain stable at high temperatures (60–90 °C) [6,7]. Wide bandgap semiconductors (photoelectrodes), such as TiO₂, WO₃ and ZnO, and synthetic sensitizers, such as ruthenium-based complex dyes, are commonly used in these solar devices [8–10], which are the fundamental elements needed to reach a considerable photon capture and current generation, and hence high photo-electron conversion efficiency (PCE) in the long term. With relation to sensitizers, high production costs, complicated synthesis and

expensive compounds are frequently needed to obtain these materials. This has been the motivation for recent investigations that explore the possibility of using natural dyes as sensitizers [11,12]. These compounds represent renewable, cheap and easily obtained dyes, with a variety of colors and high extinction coefficient (ϵ) compared to their synthetic counterparts. Natural dyes are constituted by organic components such as anthocyanins, carotenoids, chlorophylls and others. Anthocyanins have been shown to have the best interaction with the photoelectrodes mentioned above [13–15]. Energy diagrams obtained from electrochemical and optic measures have elucidated an effective charge transfer between these compounds [16,17].

Anthocyanins are a group of phenolic molecules which play an important role in the color quality of many fruits, vegetables and flowers. The color and stability of anthocyanins depend principally on the chemical structure of the different forms in which they can be found. Four different structures are strongly associated with pH, which are represented in Figure 1. Flavylium cation (red color) is the principal species at pH 1, quinoidal base (blue) at pH 2–4, and carbinol base and chalcone (colorless) at upper pH values of 6. These structures coexist in equilibrium at pH values between 4 and 6 (pH typical for fresh and processed fruits and vegetables) [18].

There are an immense variety of anthocyanins disseminated in nature. The main differences between

*Corresponding author: mario.mejia@udea.edu.co;

franklin.jaramillo@udea.edu.co

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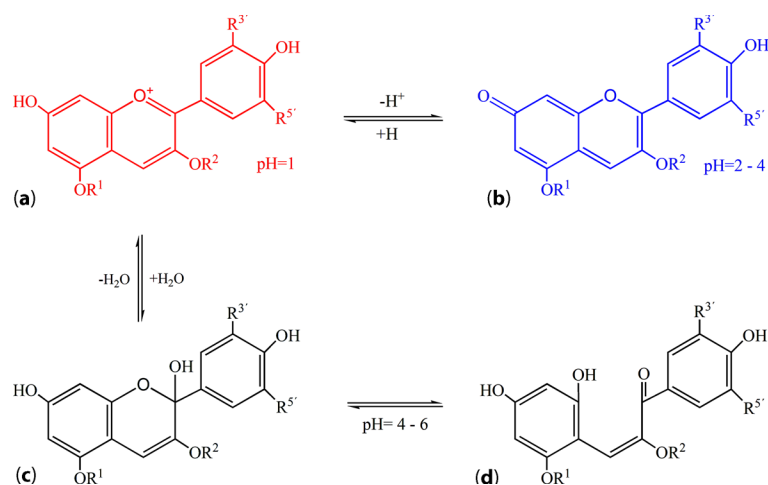


Figure 1 Chemical structures of anthocyanin at different pH values: (a) Flavilium cation, (b) Quinoidal base, (c) Carbinol base and (d) Chalcone. R can be a sugar, methyl or hydroxyl group.

them are the number of hydroxyl groups, the number and the nature of attached sugars to their structure, carboxylates (aromatic or aliphatic) to the sugar in the molecule and the position of these bonds [19], determining the electrochemical behavior of these compounds. For example, it has been reported that an anthocyanin having sugar moieties is more stable than others with only hydroxyl substituents, and hence its oxidation potential is greater [20].

In the literature there are reports of more than 500 different anthocyanins [21] of which only six are the most common: pelargonidin (Pg), peonidin (Pn), cyanidin (Cy), malvidin (Mv), petunidin (Pt) and delphinidin (Dp) [22]. The glycoside derivatives of the three non-methylated anthocyanidins (Cy, Dp and Pg) are the most common in nature, being found in 50% in flowers, 69% in fruits and 80% in colored leaves [23]. With relation to fruits and vegetables, six anthocyanins can be frequently found in these proportions: Cy 50%, Dp 12%, Pg 12%, Pn 12%, Pt 7% and Mv 7%.

Commonly, to identify the above-mentioned anthocyanins, liquid chromatography-mass spectrometry (HPLC-MS) and nuclear magnetic resonance ($^1\text{H-NMR}$) are used, but these techniques are frequently expensive or not always available, especially for detailed analysis. These limitations have stimulated many researchers to find semi-empirical methods to identify these phenolic compounds [21,24]. One of them was Brouillard [25], who proposed a practical method taking into account the absorption peak ratio between different wavelengths. Absorption at the maximum visible ($\lambda_{\text{max-Vis}}$) and ultraviolet ($\lambda_{\text{max-UV}}$) peak, 440 nm and 315 nm, are considered in this method.

It is very important to mention that isolated anthocyanins are highly unstable and very susceptible to degradation [26]. Their stability is influenced by

several factors, such as storage temperature, pH, concentration, radiation, oxygen, solvent, besides the presence of metallic ions, flavonoids, proteins and enzymes [14]. For this reason, a pool of anthocyanins from an extracted dye can be more suitable for applications where long-term stability is needed. In this phenolic system, besides the kind of anthocyanin, the anthocyanin content (TAC) is an important factor which can be determined by pH differential method [27]. Commonly, high TAC values, characteristic of a high and broad absorption peak close to 510 nm, promote chemical stability, photosensitization and hyperchromic effect, antioxidant behavior and color to a media having these phenolic compounds [14].

In this study, natural dyes extracted from 37 agro-industrial wastes were explored. Diluted acetic acid at 37 °C was the chosen extraction media. In the "dye pool" the anthocyanin content (TAC) and stability at 60 °C were determined in order to select the natural extracts for potential use in dye-sensitized solar cells. Additionally, the stability and degradation kinetics at 30 °C, 60 °C and 90 °C were evaluated outdoors and under accelerated UV conditions. Finally, dyes with the best performance in the above-mentioned tests were evaluated as sensitizers in a mesostructured solar cell.

2 EXPERIMENTAL

2.1 Dye Extraction

Agro-industrial wastes were chosen according to four aspects: availability, color, nontoxicity and appearance. With respect to the last, non-edible flowers, powders, peels and seeds were preferred. Thirty-seven potential sources were considered in this study (Table 1).

Table 1 Agro-industrial wastes used to extract the natural dyes.

Sample	Agro-industrial waste	Scientific name	Appearance
1	Turmeric	<i>Curcuma longa</i>	Powder
2	Saffron	<i>Crocus sativus</i>	Powder
3	Chili pepper	<i>Capsicum annuum</i>	Peels
4	Lulo*	<i>Solanum quitoense</i>	Peels
5	Cucumber	<i>Solanum muricatum</i>	Peels
6	Carrot	<i>Daucus carota</i>	Peels
7	Bell pepper	<i>Capsicum annuum</i>	Peels
8	Red cabbage	<i>B. oleracea var. C. f. rubra</i>	Peels
9	Sweet pepper	<i>Capsicum chinense</i>	Peels
10	Radish	<i>Raphanus sativus</i>	Peels
11	Bean pod	<i>Phaseolus vulgaris</i>	Peels/Shell
12	Eggplant	<i>Solanum melongena</i>	Peels
13	Lemon	<i>Citrus limonia</i>	Peels
14	Mountain papaya	<i>Vasconcellea pubescens</i>	Peels
15	Zapote*	<i>Quararibea cordata</i>	Peels
16	Mountain papaya seeds	<i>Vasconcellea pubescens</i>	Seeds
17	Sweet granadilla	<i>Passiflora ligularis</i>	Peels
18	Passion fruit	<i>Passiflora edulis</i>	Peels
19	Banana passion fruit	<i>Passiflora tarminiana</i>	Peels
20	Tamarillo	<i>Solanum betaceum</i>	Peels
21	Tomato	<i>Solanum lycopersicum L.</i>	Peels
22	Gulupa*	<i>Passiflora edulis f. edulis</i>	Peels
23	Jacote	<i>Spondia purpurea</i>	Peels
24	Cherry plum	<i>Prunus cerasifera</i>	Peels
25	Avocado	<i>Persea Americana</i>	Peels
26	Tangerine	<i>Citrus tangerina</i>	Peels
27	Roselle	<i>Hibiscus tea</i>	Flowers
28	Banana	<i>Genus musa</i>	Peels
29	Yellow pitahaya fruit	<i>Hylocereus megalanthus</i>	Peels
30	Mango	<i>Genus mangifera</i>	Peels
31	Cape gooseberry	<i>Physalis peruviana</i>	Peels
32	Golden zucchini	<i>Cucurbita pepo</i>	Peels
33	Jatoba	<i>Hymenaea courbaril</i>	Peels
34	Commun fig	<i>Ficus carica</i>	Peels
35	Annatto	<i>Bixa orellana</i>	Seeds
36	Beetroot	<i>Beta vulgaris</i>	Peels
37	Wild bilberry	<i>Vaccinium corymbosum</i>	Peels

*No English-language equivalent names were found.

Initially peels and seeds were rinsed with deionized water. Powders and flowers were cleaned by removing only small impurities and leaves. Subsequently, samples other than seeds were cut into small pieces of 0.50 cm x 0.50 cm. Finally, treated wastes were introduced into extraction media at 37 °C. Acetic acid (Aldrich, glacial) and water (Millipore, deionized) were used as solvents. The proposed media were chosen based on results reported in the literature [28,29], but in this work a new extraction methodology based on four sequential steps was employed: ultrasound (1 h), bain-marie (23 h at 37 °C), ultrasound (1 h) and centrifuge (3 min at 5000 RPM).

2.2 Selection Methodology of Natural Dyes

There was a fixed selection methodology with the objective of choosing the three best dyes attractive for use in photoelectrochemical applications such as DSSCs. Anthocyanin content (TAC) and UV radiation stability at 60 °C were the filters chosen. Here, it is important to mention that TAC and absorption spectrum are related to the pH differential method proposed by Wrolstad and coworkers [30], which is described below.

2.2.1 TAC

In order to determine the TAC in each extracted dye, the absorbance at 510 nm and 700 nm at two pH values (employed buffers) were chosen as response variable, since when there are anthocyanins in an aqueous media, a broad peak around 500 nm is visible in the absorption spectrum. Additionally, it is necessary to determine the TAC by the pH differential method, which is described in Equations 1 and 2 [27], where Mw is the molecular weight (g/mol), ϵ is the molar absorptivity (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, ϵ : 26900) due to the fact that it is the most common anthocyanin in nature. Absorbance values were determined in a Varian Cary 100 Spectrophotometer, using the dyes after being centrifuged at 5000 RPM for 5 minutes.

In this first filter, only dyes that had a TAC value greater than 50 mg/L were studied in the next step. It has been observed that below this value anthocyanins within natural dyes can suffer a premature oxidation by concentration effect [31].

$$A = (A_{510} - A_{700})_{pH1.00} - (A_{510} - A_{700})_{pH4.50} \quad (1)$$

$$\text{TAC (mg/L)} = (A * Mw * Df * 100) / (\epsilon * L) \quad (2)$$

2.2.2 Stability at Extreme Conditions

Natural dyes were exposed to ultraviolet radiation (0.89W/m²*nm) in a UV chamber (QUV, Q-Lab) at 60 °C for 4 hours. The objective of this test was to observe the TAC variation at extreme conditions of UV radiation and temperature.

In order to create a new filter for all dyes obtained from agro-industrial wastes, a minimum stability value called TAC₈₅ (TAC value at 85% of the initial concentration) was fixed. Natural dyes that had values below this limit after 4 hours were discarded. Dyes that met all requirements were extensively studied to determine their potential use in sensitizer solar cells (SSCs).

2.3 Qualitative Identification of Anthocyanins

With the aim of identifying the main anthocyanins within the best dye pools, the proposed method by Brouillard (peak ratio method) was used. The $\lambda_{440} / \lambda_{\text{max-Vis}}$, $\lambda_{\text{acyl}} / \lambda_{\text{max-Vis}}$ and $\lambda_{\text{max-UV}} / \lambda_{\text{max-Vis}}$ ratios were calculated. Additionally, the identification of anthocyanins by means of this method was supported by cyclic voltammetry (CV). The calculated oxidation potentials were compared with standard values reported in the literature for different kinds of anthocyanins.

The CV was conducted in a potentiostat/galvanostat (Metrohm, Autolab) using an electrochemical cell with a graphite electrode (where dye was impregnated), platinum wire (counter), 0.20 M sodium acetate as supporting electrolyte (buffer, pH 4.50) [20], Ag/AgCl (KCl_{saturated}) electrode (reference electrode) and nitrogen gas to prevent premature oxidation of samples during the test. These measures were made in triplicate.

2.4 Kinetic Study

Accurate knowledge of the degradation kinetics for the anthocyanins within the dye is essential for predicting changes that may occur either during storage or use. The conditions investigated herein assure a high compatibility with conditions generally presented in some photoelectrochemical applications such as DSSCs.

The thermal degradation of potential dyes was studied at 30 °C, 60 °C and 90 °C. Aliquots of 20 mL of dyes were put into test tubes already equilibrated in a thermostatic water bath (controlled bain-marie) at these temperatures. At regular time intervals (60, 120, and 180 min), samples were removed from the water bath and rapidly cooled by plunging into an ice water bath (3–5 °C). The analysis was conducted immediately and subsequently at regular time intervals. In

this test the measured variable was absorbance in order to determine the TAC values.

2.5 Stability Study

The stability study focused on two exposition media. Accelerated and outdoors tests were evaluated. In the first, dyes were exposed to ultraviolet radiation ($0.89\text{W}/\text{m}^2\cdot\text{nm}$, $60\text{ }^\circ\text{C}$) in a QUV UV chamber (Q-Lab) for 4 hours. With relation to outdoors testing (8 days), global radiation and temperature records were taken to know the dose values of these variables on the dyes. Data were re-collected from a Vantage Pro weather station (Davis Instruments).

Aliquots of 40 mL of dyes were put into test tubes and disposed in each media. TAC values were evaluated at 1, 2, 4, 6 and 8 hours in a UV chamber and 1, 2, 4, 6 and 8 days outdoors.

It is very important to mention that these tests, principally those outdoors, have provided a lot of information related to the behavior of dyes at normal use conditions, where variables, such as global radiation, UV index and temperature, have an important role in the degradation kinetics of these organic compounds in a solar device.

2.6 Fabrication of Solar Cells

Sensitized solar cells were fabricated and evaluated by standard procedures as reported elsewhere [32,33]. Devices were made on fluorine-doped tin oxide (FTO) coated glass (Solaronix, $10\ \Omega/\text{square}$). Initially, FTO was removed from regions under the anode contact by etching with a 2M HCl solution and zinc powder. Substrates were then cleaned sequentially in neutral soap, acetone, isopropanol, and finally at ultraviolet-ozone exposition. Then, a TiO_2 layer (electron-transporting material) was synthesized by spin-coating a mildly acidic solution of titanium isopropoxide in ethanol ($350\ \mu\text{L}$ in $10.0\ \text{mL}$ of ethanol with $0.016\ \text{M}$ HCl) sintered subsequently at $500\text{ }^\circ\text{C}$ for 45 min. Then $500\ \text{nm}$ thick mesoporous TiO_2 film was deposited by spin-coating at 2000 RPM using a commercial paste (Dyesol, 18NR-T). Posteriorly, the TiO_2 wet film was sintered at $500\text{ }^\circ\text{C}$ in air.

For the dye adsorption, the porous semiconductor electrode was heated to $450\text{ }^\circ\text{C}$ for 30 minutes to clean the semiconductor surface just prior to immersing it in the dye solution. The dyeing process was carried out overnight at room temperature. Then, the sensitized electrode was rinsed with acetonitrile. Subsequently, the counter electrode was prepared by casting a platinum precursor (Solaronix, Plastisol T) onto an FTO substrate followed by sintering at $455\text{ }^\circ\text{C}$ for 30 min. The photoelectrode and the counter electrode were

arranged in a face-to-face layout and then the space between them was filled with an iodine electrolyte (Solaronix, Iodolyte Z-100).

3 RESULTS AND DISCUSSIONS

3.1 Extraction

Dyes obtained from agro-industrial wastes are shown in Figure 2. It can be observed that there are different colors in the extracts, from the lightest (23) to the darkest (27 or 36). On the other hand, some dyes presented remnants or precipitates after being centrifuged, possibly due to the presence of nonpolar organic compounds or impurities. It is important to mention that none of the extracted dyes were filtered, only centrifuged was used, and for this reason the methodology proposed was very efficient for obtaining "clean" dyes. Only 13% of them presented residues after being centrifuged.

3.2 Natural Dye Selection

Table 2 shows the calculated TAC values of dyes from treatment of agro-industrial wastes. Approximately

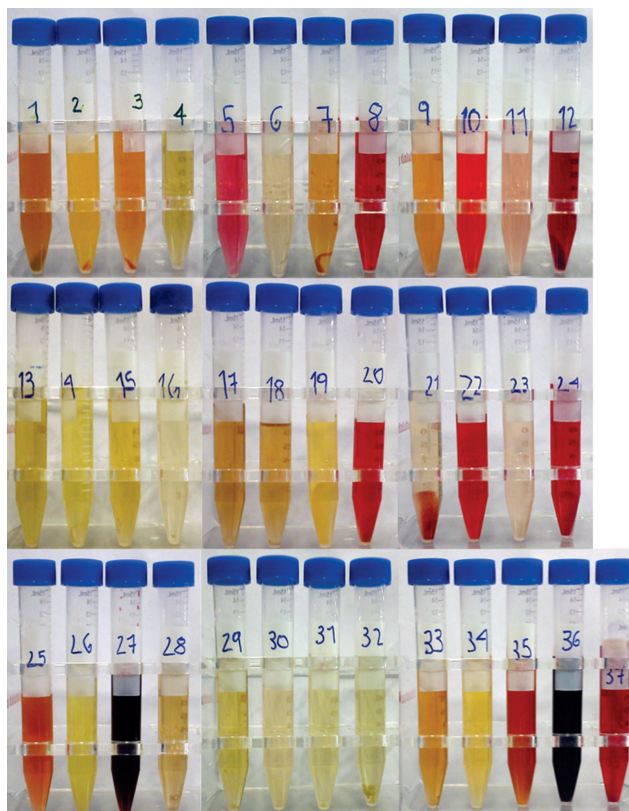


Figure 2 Appearance of the extracted dyes after being centrifuged for 3 minutes at 5000 RPM.

Table 2 TAC values of dyes extracted from agro-industrial wastes.

Sample	Agro-industrial waste	TAC (mg/L)	Maximum absorption peak (nm)	Residue after extraction ^a (%)
1	Turmeric	14.00 ± 3.17	425.28	91.18
2	Saffron	1.77 ± 0.219	433.31	98.93
3	Chili pepper	0	243.48	6.04
4	Lulo*	0	281.32	10.67
5	Cucumber	3.77 ± 3.42	317.68	3.92
6	Carrot	0	259.99	5.80
7	Bell pepper	0.28 ± 0.48	251.04	5.37
8	Red cabbage	126.81 ± 1.36	524.84	4.03
9	Sweet pepper	0	239.42	6.71
10	Radish	123.42 ± 0.13	507.86	5.20
11	Bean pod	0	259.64	18.24
12	Eggplant	16.90 ± 0.99	283.96	10.53
13	Lemon	0	320.44	11,33
14	Mountain papaya	0	263.54	7.10
15	Zapote*	0	263.54	26.09
16	Mountain papaya seeds	15.76 ± 0.91	247.48	18.55
17	Sweet granadilla	15.69 ± 0.16	275.01	17.09
18	Passion fruit	0.81 ± 0.56	267.21	29.53
19	Banana passion fruit	1.14 ± 1.73	248.06	8.44
20	Tamarillo	11.54 ± 0.27	326.74	18.67
21	Tomato	0	265.61	4.82
22	Gulupa*	128.63 ± 2.22	273.41	13.29
23	Jacote	0	270.88	22.89
24	Cherry plum	98.47 ± 0.70	278.11	4.84
25	Avocado	3.38 ± 0.05	278.11	23.24
26	Tangerine	0	327.78	13.88
27	Roselle	254.20 ± 4.37	283.27	54.37
28	Banana	0	266.64	10.18
29	Yellow pitahaya fruit	0	248.06	7.36
30	Mango*	0	263.54	26.35
31	Cape gooseberry	0	265.15	14.29
32	Golden zucchini	0	265.72	4.40
33	Jatoba	0	276.04	87.07
34	Commun fig	0	273.98	3.18
35	Annatto	0	270.88	95.40
36	Beetroot	50.98 ± 2.93	532.87	10.69
37	Wild bilberry	66.19 ± 0.55	278.11	13.10

* No English-language equivalent names were found.

^aResidue after extraction $[(\text{Initial weight})_{\text{dry}} - (\text{Final weight})_{\text{dry}}] / [(\text{Initial weight})_{\text{dry}}]$. A solid concentration of dry waste solids of 50% was used in each extraction media.

51% of the obtained dyes apparently do not present anthocyanins. From the color observation, we can say that these dyes could principally have other organic compounds such as carotenoids (orange to yellow), chlorophylls (green to yellow), betanins (violet to purple) and others [34,35]. This hypothesis can be confirmed by observing the obtained absorption spectra of each dye between 200 nm and 700 nm (*Supporting information*). It is very important to note that all dyes presented high absorption in the UV region (some dyes presented absorption in the blue) due to their high molar absorptivity (ϵ) in this region. On the other hand, some dyes presented an additional peak of around 515 nm (e.g., red cabbage), which is characteristic of the presence of anthocyanins, principally, the flavylium cation which forms due to the pH of the extraction media (pH 1–3). In general, a natural dye with presence of anthocyanins has an absorption spectra similar to a “saddle,” which has maximum absorption peaks in the UV and visible region.

It is very important to mention here that the amount of residue produced after the extraction process significantly influences its sustainability [36]. In relation to this, potential dyes (high TAC values) generated few residues compared to other agro-industrial wastes such as turmeric and saffron sources.

3.2.1 First Filter: TAC and Absorption Spectra

Analyzing all the variables shown in Table 2 and absorption spectrum for the extracted dyes (*Supporting information*), red cabbage (8), radish (10), gulupa (22), cherry plum (24), roselle (27) and wild bilberry (37) were chosen for the next selection step.

3.2.1.1 TAC_{85}

Figure 3 shows the results obtained for the stability test for dyes exposed to UV radiation at 60 °C. Clearly, red cabbage (8), radish (10) and roselle (27) were the most stable dyes and their concentration does not drop below that of TAC_{85} . These dyes presented high stability despite the strong condition of the exposition ($0.89W/m^2 \cdot nm$, 60 °C at 4 h). For this reason, these dyes were extensively studied in order to determine their potential use in DSSCs. Additionally, these results were very important for predicting the presence of highly stable anthocyanins (with substitutions of glycosyl group) in dyes 8, 10 and 27.

On the other hand, some anthocyanins can have a high antioxidant behavior. For example, cyanidins or flavones acylated or without substituted glycols present this quality [14,37]. These molecules are attacked or easily degraded to promote stabilization mechanisms

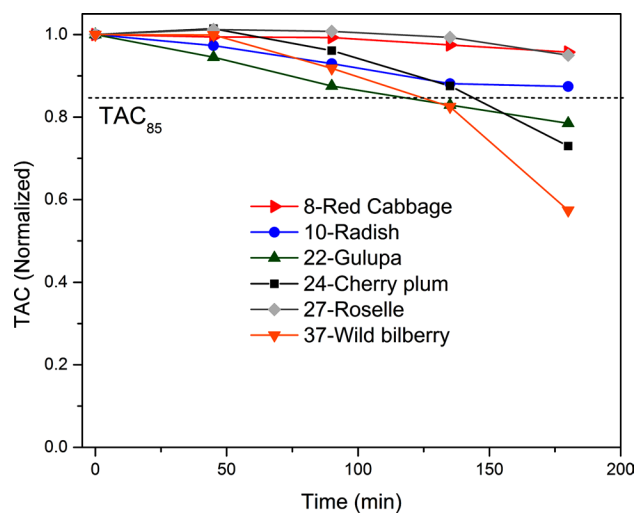


Figure 3 UV stability of partially choiced natural dyes at 60°C.

of free radicals that involve variables such as temperature and radiation [21,24]. In this regard, we could say that 22, 24 and 37 dyes could have a majority of this type of anthocyanins, susceptible to degrade within the obtained extract. For this reason, gulupa (22), cherry plum (24) and wild bilberry (37) were discarded.

3.3 Peak Ratio Analysis for Primary Anthocyanins Identification

Table 3 shows the absorption peak ratios for identification of the primary anthocyanin within the extracted dyes from agro-industrial wastes. The results were compared with reported data in the literature for standard anthocyanins [24]. It is very important to mention that there are few deviations between the values due to the presence of the other kind of anthocyanins or organic compounds in the extracted dyes. There are not any isolated anthocyanins as in the standards solutions.

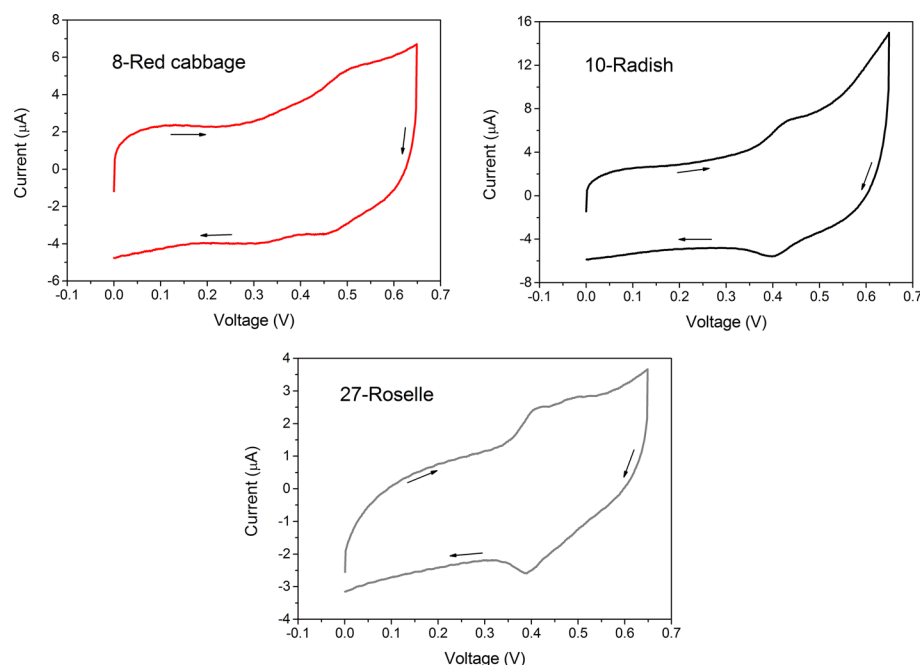
Cyanidin-3-diglucoside-5-glucoside (Cy3diG5G) and perlargonidin-3(p-coumaroyl acid)-diglucoside-5-glucoside (Pg3diG5G + pCA) were identified in red cabbage (8) and radish (10) respectively. In the case of rosella dye (27), there was no correlation between experimental and theoretical values. For this reason it was the only dye considered for the oxidation potential values calculated below.

3.4 Oxidation Potentials

Figure 4 presents the obtained voltammograms for the extracted dyes. Roselle (27) had lower oxidation potential than other dyes (E_{ox} , 0.39V). Radish and red cabbage had values of 0.42V and 0.49V respectively.

Table 3 Absorption peak ratio for potential dyes (0.1 M HCl in methanol).

Dye (name)	$\lambda_{440}/\lambda_{\max\text{-Vis}}$	$\lambda_{\text{acyl}}/\lambda_{\max\text{-Vis}}$	$\lambda_{\max\text{-UV}}/\lambda_{\max\text{-Vis}}$	Anthocyanin assignment
8 (Red cabbage)	13.00	39.72	65.44	Cyanidin-3-diglucoside-5-glucoside (Cy3diG5G) [56]
10 (Radish)	17.13	58.25	79.44	Perlargonidin-3-diglucoside-5-glucoside (Pg3diG5G + pCA) [57]

**Figure 4** Cyclic voltammetry obtained for potential dyes from agro-industrial wastes. V vs Ag/AgCl_{sat} (Fc⁺⁴/Fc⁺⁶). Scan at 1V/s.

Once again, the obtained results were compared with the literature in order to determine the most common anthocyanin within the extracted dyes. The primary anthocyanins mentioned above were reaffirmed for red cabbage and radish (Cy3diG5G and Pg3diG5G + pCA) [20,38,39]. With relation to roselle dye, its oxidation potential was very similar compared to values for delphinidin 3-sambubioside (Dp3-Sam), as has been found by other research [22,40]. Additionally, up to 85% of this anthocyanin has been found in dyes extracted from fresh rosella flowers [41,42]. This report confirms that our roselle dye has probably Dp3-Sam.

In conclusion, these results allow the prediction of the electrochemical stability of potential dyes. It can be expected that red cabbage and radish may be more stable than roselle dye. It is well known that anthocyanins with many hydroxyl groups are very unstable due to relatively easy oxidation in a protic media [43]. Additionally, if an anthocyanin has attached glycol substituents (glucose), it is more stable owing to the fact that these molecules avoid the degradation of unstable intermediaries in phenolic acid and

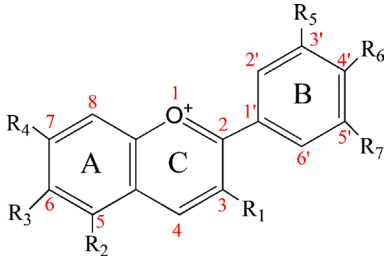
aldehyde compounds [14]. Red cabbage has a primary anthocyanin (Cy3diG5G) with 3 hydroxyl groups and 3 glucoses; anthocyanin from radish has 2 hydroxyls, 3 glucoses and one acyl group (p-coumaroyl acid). Finally, primary anthocyanin from roselle is composed of 5 hydroxyls and one glucose (sambubioside) (Table 4). From this point of view one can think that dye from radish is more stable than red cabbage, but radish has an acylated primary anthocyanin that decreases its stability, possibly due to hydrolysis [25]. This result is in agreement with the potential values obtained from CV measurements.

In general, it is then expected that the stability of the extracted dyes follows this order: red cabbage (8) > radish (10) > roselle (27).

3.5 Kinetic and Activation Energy

A summary of the calculated kinetic variables at 30 °C, 60 °C and 90 °C is presented in Table 5. This part of the work was mainly done with the aim of finding

Table 4 Structural identification of the primary anthocyanins in potential dyes. G: Glucose. pCA: Coumaric Acid. Sam: Sambubioside.



Dye (name)	Primary Anthocyanin	R1	R2	R3	R4	R5	R6	R7
8 (Red cabbage)	Cy3diG5G	2G	G	H	OH	OH	OH	H
10 (Radish)	Pg3diG5G + pCA	2G	G-pCA	H	OH	H	OH	H
27 (Rosella)	Dp3-Sam	Sam	OH	H	OH	OH	OH	OH

Table 5 Kinetic variables calculated for potential natural dyes extracted from agro-industrial wastes.

Dye	30°C			60°C			90°C			Ea (kJ/mol)
	k(min ⁻¹)	t _{1/2} (days)	R ²	k(min ⁻¹)	t _{1/2} (days)	R ²	k(min ⁻¹)	t _{1/2} (days)	R ²	
Red cabbage	1.66E-4	2.89	0.9737	5.01E-5	9.61	0.9850	7.19E-4	0.67	0.9744	40.37
Radish	2.52E-4	1.91	0.9623	3.73E-5	12.90	0.9999	5.06E-4	0.95	0.9623	40.19
Roselle	3.16E-4	1.52	0.9578	9.10E-5	5.29	0.9995	6.28E-4	0.77	0.9790	29.62

the activation energy (*Ea*) for red cabbage, radish and roselle dye. *Ea* was calculated, determining the slope in each plot shown in Figure 5. It is important to recall that this variable is proportional to the dye stability.

Clearly, it can be seen in Table 5 that there is a dependency of half-life time (*t*_{1/2}) on the temperature. At 30 °C, red cabbage is the most stable, but at 60 °C and 90 °C radish has a superior stability. The stability in these systems depends on the equilibrium between the different molecular structures that form the anthocyanins, including pH and temperature [21,24]. It is important to highlight that all obtained dyes were in a strong acid media (pH 1–3), where flavylium cation (the most stable structure) is the predominant configuration and is in equilibrium with the quinoidal base (sensitive structure to degrade). For this reason, in our systems temperature is principally responsible for the degradation of the anthocyanins within the obtained dyes. In relation to this, it has been reported that the equilibrium reactions between anthocyanin structures are endothermic in the left to right direction: Quinoidal base (blue) ⇌ Flavylium cation (red)

⇌ Pseudobase carbinol (colorless) ⇌ Chalcone (colorless). In this regard, anthocyanins in the evaluated dyes at 30 °C could have been thermodynamically promoted to quinoidal form. This hypothesis can be proven as the extracts were clearer inside the bain-marie bath at 30 °C. In this media, red cabbage dye was more stable due to the presence of three glycol groups (R1 and R2) in its primary anthocyanin, which could endothermically retard the transition to flavylium cation [14,25]. In radish, the presence of an acyl group could have affected its stability due to an increase in the susceptibility of the primary anthocyanin to suffer hydrolysis.

At 60 °C, it can be observed that major stability in the dyes was reached. Probably, flavylium cation was favored endothermically at this temperature. Color in all the dyes was more intense (presence of flavylium) compared to that observed at 30 °C. Furthermore, the obtained correlation coefficients (R²) are high enough to confirm the reliability of the hypothesis. In general, this result shows that the obtained dyes have great potential to be used in photoelectrochemical devices

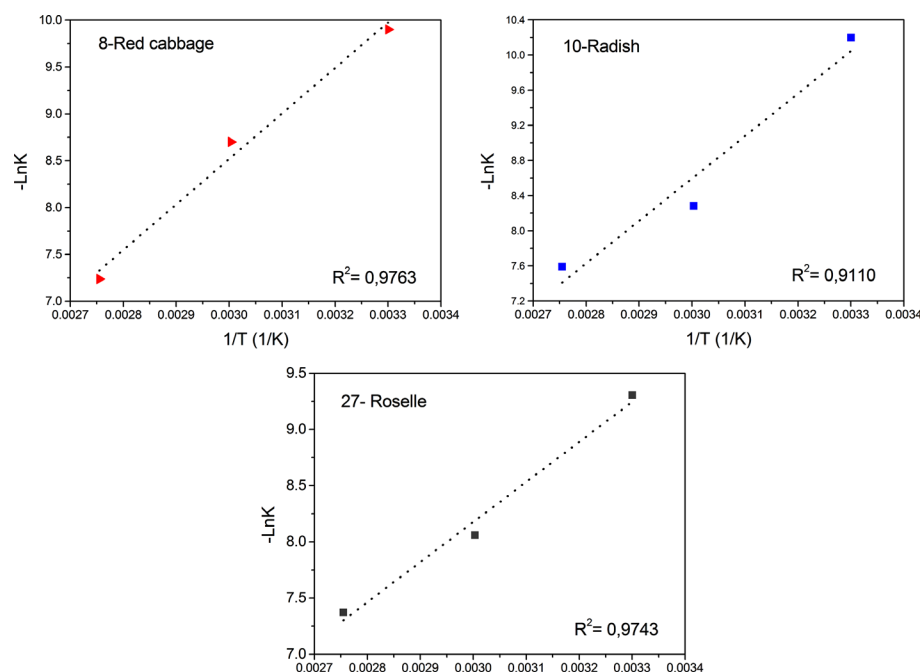


Figure 5 Arrhenius plots obtained for potential natural dyes. Dotted line (tendency line).

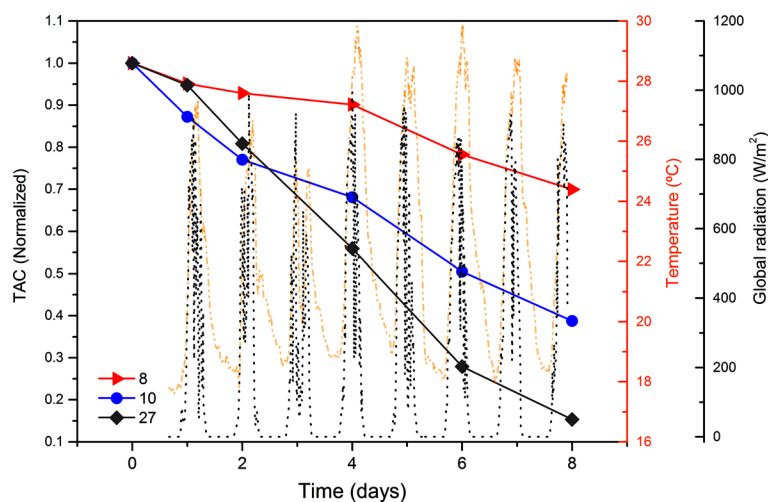


Figure 6 Stability of potential dyes at outdoors exposition: continuous spectra (temperature) and dot spectra (global radiation). Normal variations present in temperature and radiation values common in tropical climate.

at 60 °C, for example, the normal operating surface conditions in a DSSC [44].

On the other hand, at 90 °C dyes were very unstable. This was expected owing to the high probability of obtaining chalcone under this condition. This is the most unstable structure present in the anthocyanins [14].

The results shown above give very specific information on the dyes stability at different temperatures, but an estimation of global stability is represented by the activation energy (E_a). It can be seen that red cabbage (8) and radish (10) have a similar E_a , 40.37 kJ/mol

and 40.19 kJ/mol, respectively, and roselle has a lower value (29.62 kJ/mol). This result is in agreement with the hypothesis made when the kind of primary anthocyanins were determined in each potential natural dye.

Figure 6 presents the outdoor stability results for the potential natural dyes extracted from agro-industrial wastes. Red cabbage dye had better stability than other dyes during the period of study, with approximately a 30% of decrease of TAC. For radish and roselle dyes, a loss of 60% and 85% were found respectively. For these dyes, a high sensitivity to degradation during the first

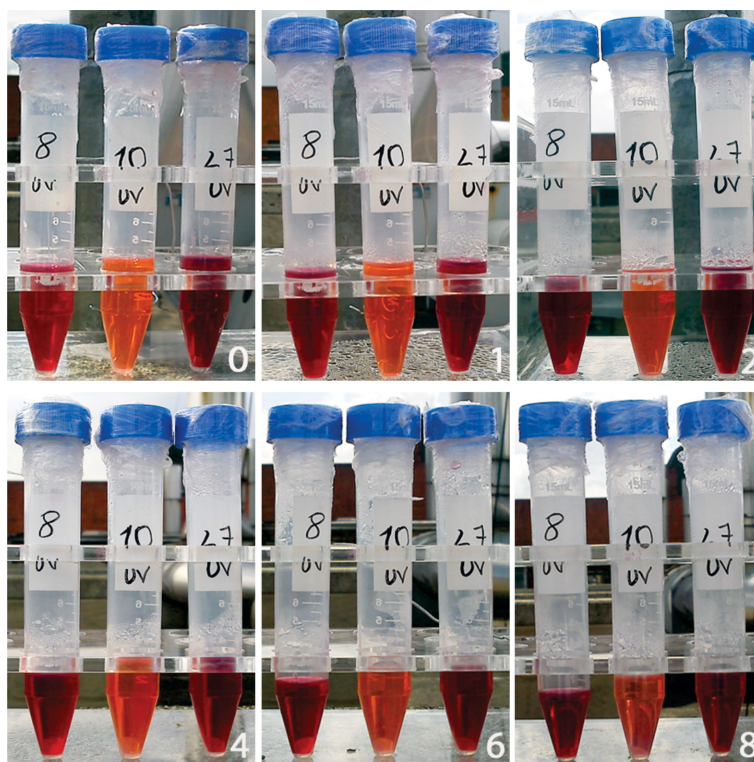


Figure 7 Colors for potential dyes after exposure outdoors (0, 1, 2, 4, 6, 8 days). 8: Red cabbage. 10: Radish. 27: Roselle.

4 days can be observed. In this period, radiation and temperature were not maxima but TAC values were affected. On the other hand, after 4 days, radiation and temperature increase markedly, presenting maxima values close to $900\text{W}/\text{m}^2$ and 30°C . Under these conditions, red cabbage started to show signs of accelerated degradation compared to the first 4 days. It is very important to mention that dyes did not present residues or precipitates during the exposition period (Figure 7). It is known that anthocyanin tends to form brown remnants when it undergoes premature degradation [24].

Figure 8 shows the performance of natural dyes under UV radiation extreme conditions. It can be seen that the degradation percentage in red cabbage was approximately 25%, 49% for radish and 55% for roselle at 4 days. Once again, red cabbage dye presented better stability, but an unusual behavior was observed after 1 hour. This can be explained due to the formation of a more stable anthocyanin as a result of the copigmentation effect common between organic elements [45]. This effect produces an increase in the absorption of anthocyanin, and for this reason TAC values would have no change. This result is in agreement with the obtained values and hypothesis from the kinetic study and primary anthocyanin identification mentioned above. The global stability of anthocyanins in red cabbage > radish > roselle.

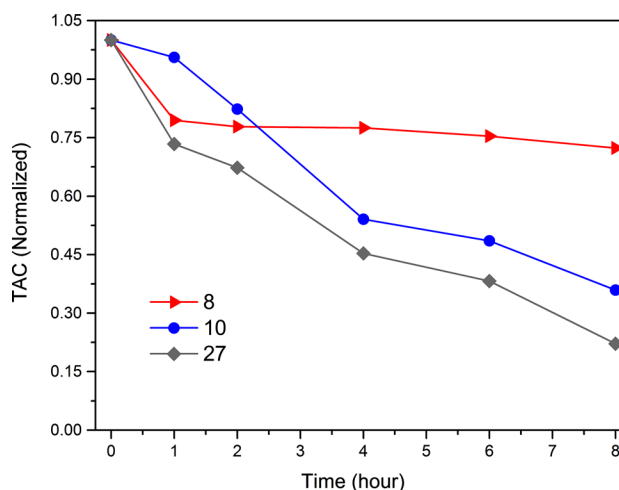


Figure 8 Stability of the potential natural dyes at accelerated UV test ($0.89\text{W}/\text{m}^2\cdot\text{nm}$, 60°C).

3.6 Copigmentation Effect

When the kinetic study was realized, TAC values were calculated in order to quantify some kinetic variables. Additionally, absorption spectra were obtained and analyzed since TAC does not give information with relation to structural and optical changes in the anthocyanins present in the extracted dyes. Figure 9 shows

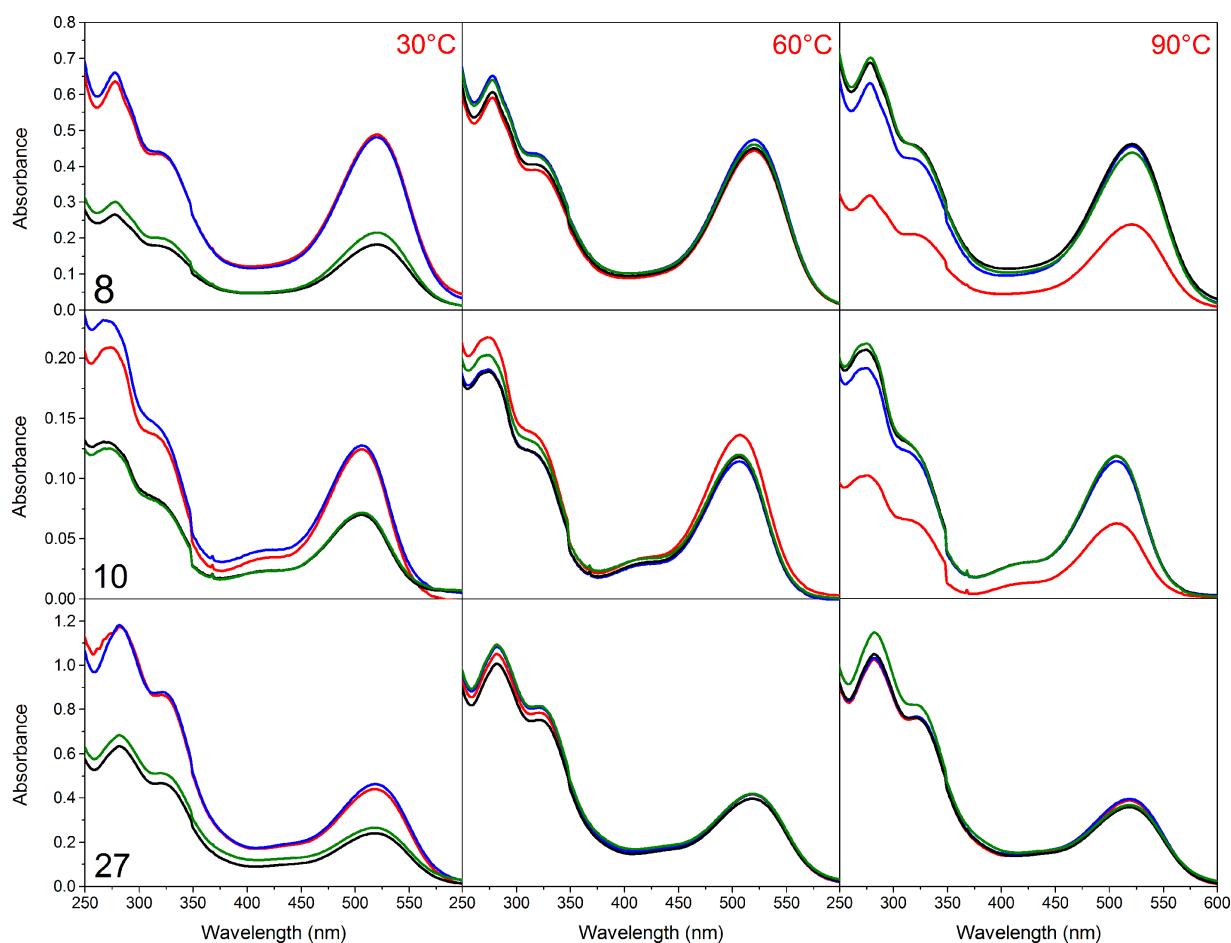


Figure 9 Absorption spectra for potential dyes at 30°C, 60°C and 90°C: 0 h (O) – 1 h (□) – 2 h (Δ) – 3 h (Start).

the obtained spectra at 30 °C, 60 °C and 90 °C for each dye evaluated at 0, 1, 2 and 3 hours. These plots are very interesting since three different behaviors can be seen in each temperature evaluated. In addition, a copigmentation effect was evidenced.

3.6.1 Degradation vs Copigmentation at 30 °C

In the first column (30 °C) of Figure 9 it can be observed that all dyes present a similar behavior during the exposition period: a little increase of absorption at 1 h, later degradation at 2 h and finally a slight copigmentation effect again (3 h). Clearly, the degradation effect is stronger than copigmentation under this condition. As was mentioned above, primary anthocyanins in our dyes at 30 °C could have been endothermically promoted to quinoidal form, which is an unstable structure compared with flavylium cation, limiting the copigmentation effect.

On the other hand, peak ratios at 270 nm, 310 nm and 525 nm were constant between the measured periods. This behavior reflects the fact that anthocyanins have not been acylated while they were degraded or mildly copigmented [46].

3.6.2 Stabilization at 60 °C by Formation of Degradation Products

As was mentioned above, flavylium cation probably is the predominant structure at 60 °C (pH 1 and endothermic equilibrium). The results shown in Figure 9 confirms this hypothesis since this ion in the anthocyanin is positively charged and is therefore a suitable candidate for the formation of complexes by charge transfer with light metals such as calcium or magnesium (commonly found in natural dyes), giving stability to media where it was formed [14]. It can be observed in the absorption spectrum in all extracted dyes at 60 °C, where there are no significant changes during the study period.

On the other hand, more stable copigmentation complexes are seen where covalent bonds can be formed between aromatic acyl groups (especially the cinnamoyl residues) linked to the sugar moieties of anthocyanins and cofactors (copigments) to provide an additional stabilization effect [47]. In this regard, in addition to the above mentioned, our dyes could be forming stable complex with degradation residues produced by the temperature effect [14], giving

Table 6 Electronic parameters of the fabricated solar cells with the extracted potential dyes.

Dye	Jsc (mA/cm ²)	Voc (mV)	FF	PCE (%)
8-Red Cabbage	2.19	428	0.78	1.63
10-Radish	1.09	424	0.70	0.72
27-Roselle	0.88	426	0.74	0.62

stabilization to the obtained extracts. This stabilization behavior has been reported by Markakis [25].

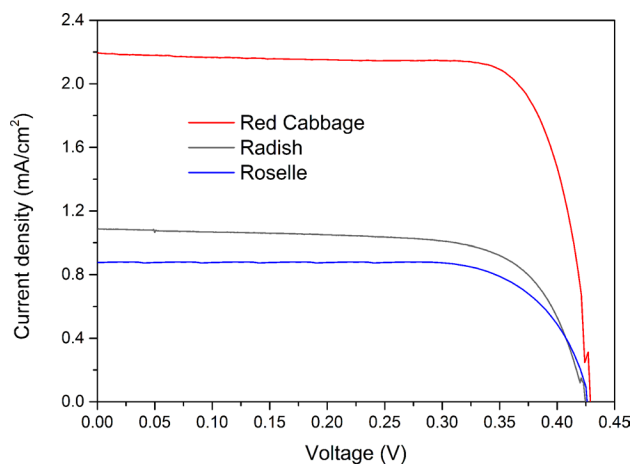
3.6.3 Solubility and Copigmentation at 90 °C

In the third column (90 °C) in Figure 9 a high copigmentation (increase in absorbance upon time) can be observed for red cabbage and radish dye. Roselle dye had a similar behavior to that at 30 °C. Not many results showing the copigmentation effect at high temperatures have been reported. High temperature has a dual contribution. It enhances the solubility of most species, but especially those copigments that have limited solubility, enhancing the pool of copigmented anthocyanins [48], and it promotes the formation of degradation products from which it can form stable complexes. For this reason an increase in the absorption spectrum can be seen. In this regard, red cabbage and radish dye may have more content of copigment or cofactors insoluble at 30 °C and 60 °C than roselle extract. However the high temperature copigmentation effect has a disadvantage, which is the high degradation kinetics of isolated anthocyanins that could not efficiently interact with cofactors. This is proven by the obtained TAC results shown in Table 5.

All results presented above show that the obtained dyes have good stability at high temperatures (60 °C and 90 °C at pH 1–3). By using the proposed dyes, photoelectrochemical devices such as dye-sensitized solar cells could result in increased performance by improving optoelectronic parameters such as ICPE and current density [10,49,50].

3.7 Solar Cell Performance

Figure 10 shows the obtained current-voltage (J-V) curves of the fabricated devices with the potential natural dyes extracted from agro-industrial wastes. It can be seen that the solar cell made with red cabbage has a remarkable behavior in comparison to the other potential studied dyes. The electronic parameters calculated from these curves, summarized in Table 6, show promising values, which surpass those reported so far for a DSSC with an effective area of 1 cm² using a natural dye [13,51]. The device fabricated with red cabbage had the best efficiency (1.63%), showing a surprising fill factor of around 78%. This

**Figure 10** Current-voltage curves of the fabricated devices with the potential natural dyes.

value without precedents confirms that the fabricated device has an efficient electronic synergy between its component materials. Additionally, the remarkable fill factor in all fabricated devices, which is very similar to the reported value in the literature when a ruthenium-complex dye is used [52], was obtained thanks to the proposed extraction media composition, which promoted an effective bond between anthocyanins and TiO₂ by means of the carboxylate group present in the acetic acid [53,54] and high extinction coefficients of the anthocyanins present in the potential agro-industrial wastes. With respect to the first, different interaction mechanisms have been proposed [55], which remark the property of the acetic acid to form different stable intermediates on TiO₂, which markedly help to have an efficient electron transfer between the LUMO of the excited dye and the conduction band (CB) of the semiconductor.

4 CONCLUSIONS

A sustainable methodology for the extraction of natural dyes from 37 agro-industrial wastes was achieved. The obtained dyes were not filtered, and the centrifugation process could be omitted due to the absence of impurities or insoluble compounds after extraction. Furthermore, few final residues from wastes were obtained. This result is very interesting since the scaling

methodology mentioned above could be cheaper than that of some processes currently employed.

Absorption spectra, TAC value and a stability study (TAC_{85}) were determined and analyzed with the aim of choosing potential dyes from agro-industrial wastes. Red cabbage (8), radish (10) and roselle (27) wastes were selected since they showed the best qualities and performance. In these, primary anthocyanins were identified by the peak ratio method and cyclic voltammetry. Cyanidin-3-diglucoside-5-glucoside (Cy3diG5G), perlargonidin-3(p-coumaroyl acid)-diglucoside-5-glucoside (Pg3diG5G + pCA) and delphinidin 3-sambubioside (Dp3-Sam) were found as the main components.

Kinetic and stability studies show that each potential dye evaluated has special qualities depending on temperature and radiation. Red cabbage was the most stable dye at 30 °C, outdoors and in UV chamber exposition. At 60 °C and 90 °C, radish was the most attractive dye. On the other hand, these dyes showed a high copigmentation effect at 90 °C, probably due to the increase solubility of copigments within the extract. An increase of 200% in the absorption was observed.

On the other hand, roselle dye shows higher antioxidant anthocyanin content compared to other dyes. This quality makes it attractive as a protective system or copigmentation promoter within other dyes studied. Finally, red cabbage and radish dyes could have potential use in DSSCs as photoelectrode sensitizer due to their stability, absorption spectra and primary anthocyanin content.

The fabricated solar devices showed great potential for dye from red cabbage as sensitizer. Roselle and radish dye within DSSC architecture promoted lower efficiencies, but within the normal range reported for natural dyes. Here, it is important to mention that the evaluated effective area was 1 cm², which presents the opportunity to fabricate these solar devices at a larger scale.

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Supporting Information