

## GREEN SEAWEEDS EXTRACT AS CO-SENSITIZER FOR DYE SENSITIZED SOLAR CELLS

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**Abstract:** The row extract of ethanol soluble compounds from the green alga *Enteromorpha intestinalis* was used as source for chlorophyll pigments in the sensitization and co-sensitization of TiO<sub>2</sub>-based Dye Sensitized Solar Cells (DSSCs). We used two techniques for co-sensitization (the successive adsorptions of dyes, respective the cocktails of dyes) and the characteristics of DSSCs were studied having in view different pHs of the extracts. The results for DSSCs based on co-sensitized TiO<sub>2</sub> photoanodes, obtained in diverse pH conditions, were compared with those for DSSCs based on substrates sensitized by a single source of pigments. The DSSCs fabricated using photoanodes sensitized with a cocktail of green seaweeds and red cabbage extracts, in basic medium, have higher value for efficiency, compared to green seaweeds, respective red cabbage extracts in the same conditions, and the fill factor was remarkable high (0.795). Thus, the co-sensitization by cocktail method may be a proper technique to enhance the light harvesting capability of natural dyes based DSSCs.

**Keywords:** *anthocyanins, chlorophyll, co-sensitization, dye-sensitized solar cells, Enteromorpha intestinalis, green seaweeds*

## INTRODUCTION

For several decades, the interest of many scientists was focused in the research concerning safe and clean energy resources; between these resources, the solar energy is much important. After the first report published by M. Grätzel in 1991 [1], the Dye-Sensitized Solar Cells (DSSCs, Grätzel cells) quickly became very interesting, both for academic and industrial research, as a cheap source of clean energy and a real solution for renewable energy.

A DSSC consists of an electrode with a porous layer of a nanocrystalline wide band gap semiconductor, such as  $\text{TiO}_2$ , sensitized with a light absorbing dye, a redox electrolyte (e.g.  $\text{I}_3^-/\text{I}^-$ ) and a counter electrode (for instance platinized conductive glass). The working principle of the device is based on light absorption in the dye anchored to the  $\text{TiO}_2$  nanoparticles, followed by transfer of the resulting photoelectron from the excited level of the dye into the conduction band of  $\text{TiO}_2$ , and through the electrode into the external circuit. The electrolyte facilitates the transport of the electron and the regeneration of the sensitizer, through reduction of the triiodide ion at the counter electrode, followed by oxidation of the iodide ion at the dye [2, 3].

The mechanism of DSSCs can be described as an artificial photosynthesis process, which reminds the natural photosynthesis involving the light-energy absorption and charge separation [4, 5]. This comparison has determined the researchers to test the chlorophylls as pigments for DSSCs [6], and by extrapolation other vegetal pigments, as cheap and non-toxic dyes; for that purpose, the most studied vegetal pigments are chlorophylls, anthocyanins, and betalains [7 – 11 etc.], extracted from different sources like fruits, vegetables, leaves, flowers and algae [e.g. 12 – 14]. The cost-effectiveness of DSSCs (defined as the ratio between the conversion efficiency and the cost of the dye) using, for instance, anthocyanins extracted from red cabbage, is 50 times larger than in the case of ruthenium complexes [15].

Between the chlorophylls, chlorophyll *a* (Chl-*a*) does not adsorb efficiently on  $\text{TiO}_2$  due to the weak interaction of its ester and ketocarbonyl groups with the hydrophilic oxide surface, while chlorophylls *c* (Chl-*c*, including Chl-*c1* and Chl-*c2*) have the terminal carboxyl group, connected to the porphyrin macrocycle through a conjugated double bond, therefore must bind strongly to  $\text{TiO}_2$  by means of the carboxylic anchoring group, to ensure efficient electron injection into the  $\text{TiO}_2$  conducting band and to prevent gradual leaching by the electrolyte. It was demonstrated that the Chl-*c1* and Chl-*c2* absorb solar radiation strongly, with absorption bands in the UV – visible region, covering a broad range of wavelengths. Therefore, they have the potential to efficiently inject electron from the porphyrin macrocycle to  $\text{TiO}_2$ . The most abundant photosynthetic species containing Chl-*c*, generally a mixture of Chl-*c1* and Chl-*c2*, belong to seaweeds and marine plankton [16, 17].

One of the most important and challenging factors attributed to the lower efficiency of the DSSC is the lower optical absorption window (400 – 800 nm) of dyes, which is smaller compared to crystalline silicon (500 – 1100 nm). Among the key elements of DSSC, sensitizing dyes play the most important role in photon harvesting and an optimal sensitizer for such application should be panchromatic, absorbing all the light from visible to NIR wavelength region, which is presently difficult using a single dye. A probable solution for this problem is the use of two different dyes absorbing in the lower and higher wavelength regions (co-sensitization, co-pigmentation) and several

reports about the enhancement of the DSSC performances using two or more dyes in a dye-cocktail solution were published [18]. In the co-sensitization process there are different approaches, normally “molecular cocktail” approach and “band-gap cascade” approach [19, 20]; the successive adsorptions of dyes (double layered co-sensitization, DL) is a convenient experimental technique for pigments which have different adsorption rate onto semiconductor, but some studies revealed the formation of dye double layer as well from a dye mixture, by a simple dipping process, when it is used a combination of one dye with faster diffusion along with weak binding on TiO<sub>2</sub> surface and another dye with slow diffusion along with strong binding [18, 21].

In our study, we sensitized the semiconductor layer of DSSCs with two natural extracts, meaning an extract of chlorophylls from green seaweeds (*Enteromorpha intestinalis*, harvested from the Romanian Black Sea coast), and an extract of anthocyanins from red cabbage. The considered co-sensitization involved two methods, namely the successive adsorptions of dyes and the dye-cocktail. The characteristics of DSSCs containing co-sensitized photoanodes were compared with those obtained for the DSSCs with photoanodes sensitized by a single extract. The mixture of natural dyes as source of pigments for DSSCs was previously reported for other vegetal extracts (*e.g.* mixtures of pigments from red-cabbage, curcumin, and red-perilla [15]; chlorophyll from pomegranate and anthocyanins from mulberry [22], respective from wormwood and red cabbage [23]); the method was found to be a solution for promoting the light harvesting and enhancing the photoelectric conversion of dye-sensitized solar cells.

*Enteromorpha intestinalis* (taxonomic synonym of *Ulva intestinalis* Linnaeus) is a green alga from the Black Sea, being a potential source of chlorophylls and also of many other compounds, with various applications. The macroalgae show a broad range of applications and their importance in several sectors is steadily increasing worldwide, but they are an underexploited resource in the photovoltaic technologies [15, 24, 25]. Our literature review has suggested that the extracts from green algae (*i.e.* *Enteromorpha intestinalis*) were not used previously as co-pigment for DSSCs.

## MATERIALS AND METHODS

All the solvents and the chemicals employed for the experiments were of reagent or spectrophotometric grade.

### Preparation of vegetal extracts

The extracts were obtained from fresh biological materials (green algae and red cabbage).

The green algae extract was prepared as follows: 3 g of green algae were mixed in a mortar with 5 g of clean sand. 30 mL of ethanol were added in small portions over the mixture. The red cabbage extract was prepared as follows: 30 mL of water were added over 5 g of clean red cabbage (small pieces). The mixtures were kept for 24 hours in dark places, and then filtered. The pH of the red cabbage extracts was adjusted by adding HCl 1M (pH = 1), respective NaOH 1M (pH = 8).

All resulted solutions were protected from direct light exposure.

## Preparation of photoanodes

The conductive glass substrate consists of a soda lime glass sheet of 2.2 mm thickness, with a conductive layer of F-doped  $\text{SnO}_2$  and sheet resistance of  $15 \Omega \cdot \text{cm}^{-2}$  (Solaronix), having an optical transmission greater than or equal to 80%, in the 400 - 700 nm region. The  $\text{TiO}_2$  porous film was obtained by using the sol-gel method, starting from the commercial anatase  $\text{TiO}_2$  nanopowder (P25, Sigma-Aldrich) and titanium isopropoxide (Sigma-Aldrich) [26]. The conductive glass substrates were pre-treated by immersing in a  $\text{TiCl}_4$  (Sigma-Aldrich) 40 mM solution and kept for 40 min at 70 °C, to increase the short-circuit photocurrent [27]. The FTO substrates were subject to the coating of a porous film by the “doctor-blade” technique with  $\text{TiO}_2$  paste. Layers were sintered at 450 °C for 1 h. The resulting photoanodes were immersed in a  $\text{TiCl}_4$  40 mM solution, kept overnight and sintered at 450 °C for 1 h [28].

The pigment N719 (Ruthenium 535 – bis TBA,  $(\text{Bu}_4\text{N})_2[\text{Ru}(4 - \text{carboxy} - 4' - \text{carboxylato} - 2, 2' - \text{bipyridine})_2(\text{NCS})_2]$ ), from Solaronix, was dissolved (60 mg) in 100 mL of anhydrous ethanol [28], in order to fabricate a reference DSSC. The photoanode plates were stained in N719 dye solution by soaking for 2 h at 70 °C. The non-adsorbed dye were washed away with proper solvents until the rinse liquid was colorless and then dried at 80 °C for 30 min.

The photoanodes designed for natural dye based sensitized solar cells were prepared using both the sensitization with the chlorophylls and anthocyanins extract, and the co-sensitization with chlorophylls and anthocyanins.

For the sensitization with chlorophylls, respective with anthocyanins, the titania plates were immersed in the filtered extracts at room temperature and kept overnight, in order to allow the dye molecules sufficient time for adsorption. The non-adsorbed dyes were washed away with ethanol until the rinse liquid was colorless and then dried at 40 °C for 60 min.

For the co-sensitization we used two techniques, namely the successive adsorptions of dyes and the cocktails method.

The successive adsorptions of dyes consisted in the double immersion of the plate in two different dyes solutions [21]. The titania plates were first immersed in the chlorophylls extract, as described above, and dried without heating. After that, the titania plates were immersed in the anthocyanins extracts ( $\text{pH} = 1$ ), and were kept overnight, for the adsorption of next dye layer. The non-adsorbed dye was washed away with ethanol until the rinse liquid was colorless and then dried at 40 °C for 60 min.

The cocktails were prepared by mixing the vegetal extracts in a volumetric ratio of 1:1; for basic medium the cocktail  $\text{pH}$  was afterward adjusted by adding NaOH 1M ( $\text{pH} = 8$ ). The titania plates were immersed in the cocktails, at room temperature, and kept overnight, in order to allow the dye molecules sufficient time for adsorption. The non-adsorbed dyes were washed away with ethanol until the rinse liquid was colorless and then dried at 40 °C for 60 min.

## Manufacture of DSSCs

Platinum counter electrodes were prepared by spreading a few drops of 5 mM  $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$  solution in 2-propanol on the FTO glass, followed by drying at 100 °C for 10 min and then at 385 °C for 30 min [29].

The electrolyte solution for natural pigments DSSCs was prepared dissolving KI (0.5 M) and I<sub>2</sub> (0.05 M) in mixed solvents of ethylene glycol and acetonitrile (4:1 in the volume ratio) [30]. The Iodolyte TG - 50 (50 mM of tri-iodide in Tetraglyme) electrolyte, from Solaronix, was used for the N719 DSSCs.

The DSSCs were assembled following the procedure described in the literature [31], the catalyst-coated counter electrode being placed on the top, so that the conductive side of the counter electrode faced the TiO<sub>2</sub> film. The iodide electrolyte solution was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

### Characterization and measurements

The UV-VIS absorption spectra of dye solutions and dyes adsorbed onto TiO<sub>2</sub> surface were recorded in the range 200 – 900 nm, respectively 220 – 850 nm, on a Jasco V 550 spectrophotometer, either in quartz cuvettes in absorption mode or in an integrating sphere.

The electro-optical parameters of the DSSCs, the short circuit current,  $I_{SC}$ , the open circuit voltage,  $V_{OC}$ , the fill factor,  $FF$ , and the photovoltaic conversion efficiency,  $\eta$ , were measured under AM 1.5 G standard conditions (1000 W/m<sup>2</sup>) at 25 °C, using a homemade class A small area solar simulator [32]. The cell surface was exposed to light through a circular slit of 10 mm diameter, resulting in a useful area of about 0.785 cm<sup>2</sup>. The current and voltage values were measured using two digital bench multimeters (Mastech MS8050) and a decadic resistance box. All measurements were made at intervals of 45 s, allowing for each reading to stabilize.

We compared the performance of natural extracts based DSSCs to the standard DSSCs prepared with N719 dye, which lead to a solar energy conversion efficiency of 2.26 % [9, 33, 34].

## RESULTS AND DISCUSSION

The performance of vegetal pigments as co-sensitizers for DSSCs was studied by varying the co-sensitization method and also the  $pH$  of pigments solutions, for the cocktails method. Furthermore, the co-sensitized DSSCs characteristics were compared with those of single vegetal pigment DSSCs.

### Characterization of the extracts and cocktails

We used three red cabbage extracts, with different values of  $pH$ : (i)  $pH = 1$ , adjusted with HCl 1M (RC1); (ii)  $pH = 5.4$ , natural  $pH$  (RC2); (iii)  $pH = 8$ , adjusted with NaOH 1M (RC3). The green algae extract (GA) was used without the adjustment of  $pH$ . We also used three cocktails: (i) a mixture of the green algae extract with a red cabbage extract ( $pH = 1$ , RC1), having the resulted  $pH = 3$  (CC1); (ii) a mixture of the green algae with a red cabbage extract ( $pH = 5.4$ , RC2), having the resulted  $pH = 5.8$  (CC2); (iii) a mixture of the green algae extract with a red cabbage extract ( $pH = 8$ , RC3), the value of  $pH$  being adjusted at 8 with NaOH (CC3).

The extracts and their mixtures were analyzed by UV-Vis spectroscopy. The maxima of absorptions and their assignments are shown in Table 1.

**Table 1.** The assignment of absorption maxima in the UV-Vis spectra of the pigment solutions (vegetal extracts and their mixtures) and the pigments adsorbed onto TiO<sub>2</sub> layer

Pigment solution	Absorption maxima [nm]	Adsorbed pigment	Absorption maxima [nm]	Assignments
GA	275; 311	PA-GA	-	aromatic compounds
	420; 448		413	chlorophylls
	659		663	chlorophylls
RC1	276; 325	PA-RC1	-	aromatic compounds
	520		548	anthocyanins
RC2	278; 323	PA-RC2	-	aromatic compounds
	555		568	anthocyanins
RC3	278; 310	PA-RC3	-	aromatic compounds
	602		606	anthocyanins
-	-	PA-DL	406	chlorophylls
	-		553	anthocyanins
CC1	338	PA-CC1	-	aromatic compounds
	-		422	chlorophylls
	534		550	anthocyanins
CC2	420	PA-CC2	400	chlorophylls
	672		572	anthocyanins
CC3	399	PA-CC3	399	chlorophylls
	603; 663		578	anthocyanins

It was demonstrated that the absorption spectrum of a green leaf extract containing a mixture of Chls-*a* and *b* and total carotenoids is dominated by the absorption of Chl-*a* at 428 nm (blue) and 661 nm (red) [35]. Chl-*b* and the carotenoids absorb broadly in the blue region (400 to 500 nm). The chlorophylls of the *c* family can be determined at 436 nm (Chl-*c1*), 440 nm (Chl-*c2*), 447 nm (Chl-*c3*) [36].

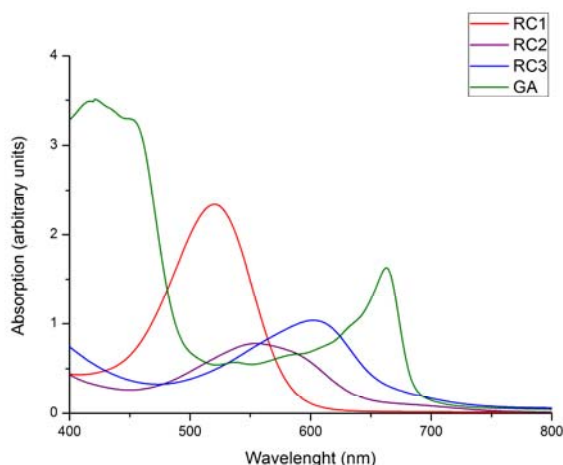
The absorption spectrum of the studied green algae extract consists in a broad band, probably a mixture of chlorophylls and carotenoids, with two maxima at 413 nm, respective 663 nm; the most abundant chlorophyll seems to be Chl-*a*. An absorption band which may be assigned to Chls-*c* is partial overlapped to those assigned to Chl-*a*, centered at 420 nm, and appears as a shoulder at 448 nm. The absorption spectra reflected that pigments in red cabbage extract consist mainly of anthocyanins (480–630 nm) [37]. The electronic spectra of anthocyanins are *pH* dependent, the absorption maxima moving to higher wavelengths with increasing of *pH*. Thus, the anthocyanins extract is red at *pH* = 1 – 3, turns into purple (*pH* = 6 – 7) and then in blue (*pH* = 7 – 8) [38].

It is important a correlation between the composition of the studied extracts and the *pH*; thus, in acid medium, the anthocyanins concentration is not only higher in comparison with other media, but the ratio between anthocyanins and other soluble components (aromatic compounds which absorb in UV domain) is also high (1:0.90:1.16). In other *pH* conditions the concentration of anthocyanins decreased compared to those of aromatic compounds (in neutral medium 1:4.44:5.57; in basic medium 1:2.56:2.94); the explanation may be the difference between the concentration of the colored and the colorless species (a carbinol pseudobase and a chalcone). Thus, at *pH* values over 4, four structural forms of the anthocyanins coexist: flavylium cation, anhydrous quinoidal

base, colorless carbinol base and the pale yellow chalcone [39]. The colorless compounds, in equilibrium with colored anthocyanins, may interfere with them in the process of adsorption onto titania surface; on the other hand, these compounds may act as antioxidants and can preserve the anthocyanins.

The cocktails spectra are also *pH* dependent (Table 1). In acidic medium the spectrum is dominated by the anthocyanins absorption band (534 nm); a very strong absorption band in the UV domain may be assigned to aromatic compounds which were extracted from vegetable materials [40]. In neutral medium (*pH* = 5.8) the band assigned to chlorophylls is more intense compared to those assigned to anthocyanins (572 nm), but in the basic medium the most intense band is assigned to anthocyanins. In the electronic spectrum of CC3 it can be observed a band at 663 nm, which is not found in the spectrum of adsorbed pigments. The band may be assigned to the compounds which can result by degradation of anthocyanins; in the RC3 spectrum this band may be overlapped by those assigned to anthocyanins. Another explanation may consist in the dependence of the anthocyanins spectrum on the extraction solvent (water for red cabbage, water and ethanol in the cocktails).

The absorption spectra of the extracts (Figure 1) show that their mixtures can be more efficient in the sensitization of photoanodes for DSSCs, because they absorb in the lower and higher wavelength regions [18].



**Figure 1.** The electronic spectra of the green algae (GA) and red cabbage (RC) extracts

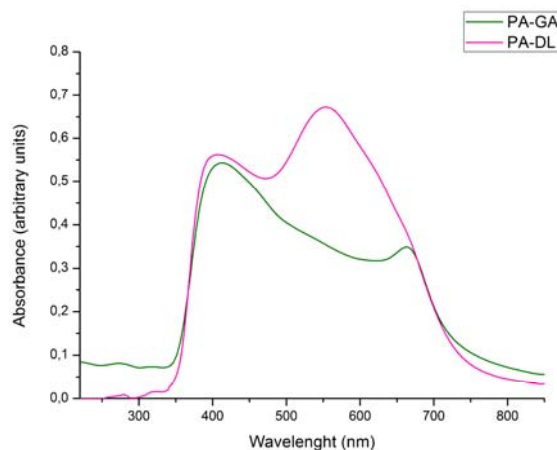
### Characterization of the photoanodes

We used in our study photoanodes prepared as follows: (i) photoanodes sensitized with chlorophylls from green algae extract (PA-GA); (ii) photoanodes co-sensitized with chlorophylls and anthocyanins, by successive adsorptions of dyes (PA-DL); (iii) three types of photoanodes sensitized with cocktails (PA-CC1, PA-CC2, PA-CC3).

For comparison, we also used three types of photoanodes sensitized with anthocyanins from red cabbage, namely (i) photoanodes sensitized with the anthocyanins extract with *pH* = 1 (PA-RC1), (ii) photoanodes sensitized with the anthocyanins extract with *pH* = 5.4 (PA-RC2), (iii) photoanodes sensitized with the anthocyanins extract with *pH* = 8 (PA-RC3).

The adsorption of pigments onto semiconductor layer was estimated using the UV-Vis spectroscopy (Table 1).

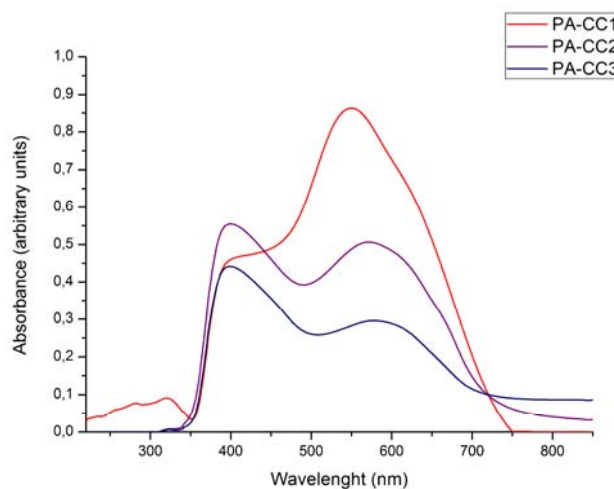
The electronic spectra of pigments adsorbed onto titania surface through co-sensitization method were compared with those of individual adsorbed pigments. For example, in Figure 2 is shown a comparison between the electronic spectra of adsorbed chlorophylls (PA-GA) and double layered adsorbed pigments (PA-DL).



**Figure 2.** The electronic spectrum of chlorophylls adsorbed onto  $\text{TiO}_2$  layer (PA-GA) in comparison with the spectrum of pigments adsorbed onto  $\text{TiO}_2$  layer by the successive adsorptions of dyes (PA-DL)

Two absorption maxima can be seen in the electronic spectrum of the adsorbed pigments onto PA-GA photoanode, and both may be assigned to Chl-*a*; the absorption in the blue domain is stronger compared with those in the red domain. In the electronic spectrum of pigments adsorbed onto PA-DL, the band assigned to Chl-*a* in the red domain was overlapped by the band assigned to anthocyanins, which is stronger. It deserves to be noted that the absorbance for the anthocyanin band is higher compared with those assigned to Chl-*a*, despite the chlorophylls were adsorbed first and thus, the anthocyanins were adsorbed onto a surface which was already covered by the chlorophylls, in consequence the number of adsorption sites decreased.

The electronic spectra of the pigments adsorbed from cocktails onto  $\text{TiO}_2$  layers are dependent of the solution pH (Figure 3).



**Figure 3.** The electronic spectra of pigments adsorbed from cocktails onto  $\text{TiO}_2$  layers

The adsorption of the pigments onto the semiconductor layers may depend on many factors, involving both the  $\text{TiO}_2$  properties and the dye structure (like anchoring groups, the structure of molecule, the distribution of electrons in molecular orbitals, etc.) [5].

It was demonstrated that the condition of peptization for the mesoporous nanocrystalline  $\text{TiO}_2$  films influence the characteristics of DSSCs. Thus, base-catalyzed conditions led to mesoporous  $\text{TiO}_2$  that gave slower recombination in DSSCs and higher  $V_{\text{OC}}$  but a reduced dye adsorption compared with the acid-catalyzed  $\text{TiO}_2$  [41].

In our study we reached similar conclusions for the influence of the acido-basic character of pigments solution. Thus, despite all cocktails were prepared in the same volumetric ratio, from solutions of the same concentration, the ratio of absorption assigned to chlorophylls to those assigned to anthocyanins is lower in acidic medium compared with neutral and basic media, meaning a higher amount of anthocyanins. Though, the characteristics of DSSCs sensitized by basic cocktail were superior to those sensitized in acidic and neutral media, and the  $V_{\text{OC}}$  values (Table 2) are highest in basic media, both for anthocyanins extracts and cocktails. The absorbance assigned to anthocyanins and chlorophylls are comparable in neutral medium and the minimum of the ratio was achieved in basic medium, although the anthocyanins have a higher ability to be adsorbed onto  $\text{TiO}_2$  in comparison with chlorophylls.

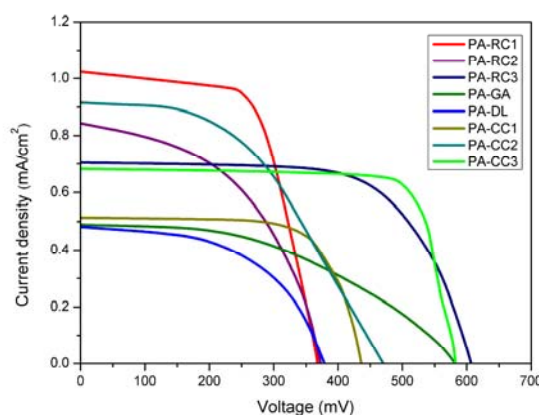
The bands assigned to anthocyanins have similar position in the spectra of adsorbed pigments, both in neutral and basic media, probably because of the interaction between the titania surface (acidified in the reaction between  $\text{TiCl}_4$  and  $\text{H}_2\text{O}$ , during the treatment of  $\text{TiO}_2$  film) and the extract. The adsorbed anthocyanins seems to have the same color (hence the similar structure), both in PA-CC2 and PA-CC3. In the electronic spectra of adsorbed pigments, for the cocktail obtained in acidic medium, they are also absorption bands in UV domain, which may be assigned to aromatic compounds.

### Characterization of DSSCs

The typical values resulting from the electro-optical measurements performed on DSSCs fabricated with vegetal pigments are displayed in Table 2 and illustrated as I-V curves in Figure 4.

**Table 2.** Electro-optical parameters: short circuit current ( $I_{\text{SC}}$ ), open circuit voltage ( $V_{\text{OC}}$ ), current density ( $J$ ), maximum power ( $P_{\text{max}}$ ), fill factor ( $FF$ ), and photovoltaic conversion efficiency ( $\eta$ ) of typical DSSCs measured under standard illumination conditions

Photoanode	$I_{\text{SC}}$ [mA]	$V_{\text{OC}}$ [mV]	$J$ [ $\text{mA}\cdot\text{cm}^{-2}$ ]	$FF$	$\eta$ [%]
PA-GA	0.384	582	0.488	0.460	0.131
PA-RC1	0.804	368.18	1.023	0.650	0.245
PA-RC2	0.662	372.79	0.843	0.549	0.173
PA-RC3	0.553	606.9	0.704	0.661	0.282
PA-DL	0.378	378.98	0.481	0.539	0.098
PA-CC1	0.403	436.27	0.513	0.704	0.158
PA-CC2	0.719	470.61	0.915	0.464	0.200
PA-CC3	0.536	582.9	0.682	0.795	0.316



**Figure 4.** Current-voltage curves for typical dye-sensitized solar cells fabricated with the photoanodes sensitized and co-sensitized with the extracts of green algae and red cabbage, measured under standard illumination conditions

To estimate the suitability of the co-pigmentation methods used in this study, we can compare the characteristics of DSSCs. Thus, by comparison of the electro-optical parameters values determined for PA-GA, respective PA-DL based DSSCs, it appears that the fill factor recorded an improvement (from 0.460 to 0.539) by the successive absorption co-sensitization, although the efficiency of cell was lower (but comparable) to those of mono-layered reference (PA-GA).

The efficiency of DSSCs based on photoanodes sensitized by cocktails method was higher (PA-CC3), comparable (PA-CC2) or lower (PA-CC1) in comparison with those sensitized with red cabbage extracts, in similar conditions of pH. Excepting the sensitization in neutral medium (PA-CC2), the co-sensitization increased the FF values, the value for basic medium (PA-CC3) being remarkable high (0.795). Furthermore, the fill factor value is preserved in time; e.g., after eight months the value of fill factor is almost the same ( $FF = 0.763$ ), while the efficiency value decreased to third ( $\eta = 0.108\%$ ).

A comparable dependence of the extracts pH can be observed for the DSSCs sensitized with red cabbage extract and it was also highlighted in our previous studies for red cabbage juices [14]. The higher values in basic or in acidic media may also be explained by the hydrolysis of functional groups from the organic compounds in red cabbage extract, especially the alkaline hydrolysis of ester groups in reaction with NaOH. The hydrolysis makes the molecules more able to be coordinated to  $\text{TiO}_2$  surface, mainly in basic medium when the hydroxyl and/or carboxyl groups may be also deprotonated. A proper and strong linkage to the semiconductor results in better performances for solar cells.

In consequence, the use of the co-pigmentation by cocktails methods improved the efficiency for DSSCs both in acidic, neutral and basic media, but the better results were obtained in basic medium, namely an enhancement of efficiency with 141 % compared to green algae extract, and with 12 % compared to red cabbage extract, in the same conditions.

Chand and Lo reported the enhancement of the photoelectric conversion efficiency for mixed dye-sensitized solar cell (0.722 %) compared to the efficiency of DSSCs based on pomegranate leaf extract (chlorophylls source, 0.597 %) and mulberry fruit extract

(anthocyanins source, 0.548 %) [22]. An enhancement of the DSSCs efficiencies was also achieved by mixing anthocyanins from red cabbage and chlorophylls from wormwood, meaning the increasing of efficiency with 140 % compared to chlorophylls and 72 % compared to anthocyanins [23].

## CONCLUSION

In our research we tested a row ethanolic extract from green seaweeds (*Enteromorpha intestinalis*) as pigment source for DSSCs, both for pigmentation and co-pigmentation of photoanodes; we experienced the co-pigmentation of photoanodes by chlorophylls (from green algae extracts) and anthocyanins (from red cabbage extracts) using two methods, namely the successive adsorptions of dyes and the cocktails method, in different conditions of pH. For comparison, we also studied the characteristics of DSSCs sensitized with green seaweeds extract, and respective red cabbage extracts, in similar conditions.

We can highlight the following conclusions:

- The *Enteromorpha intestinalis* alga proved to be a good source of chlorophylls, including Chl-*c*, which has the higher ability to be coordinated to TiO<sub>2</sub> surface. However, the anthocyanins have a greater capacity to be adsorbed onto TiO<sub>2</sub> surface in comparison with chlorophylls.
- The co-sensitization by successive absorption of pigments lead to a broad absorption band (350 – 750 nm), by joining the band assigned to chlorophylls with those assigned to anthocyanins, but the efficiency of DSSC remains low, comparable with those of the green algae based DSSC.
- The electronic spectra of cocktails and adsorbed pigments (and in consequence the composition) are pH-dependent.
- The influence of the pH in the peptization process reported previously for TiO<sub>2</sub> paste may be extrapolated for the influence of the pigment solution pH.
- The co-pigmentation by cocktails method, especially in basic medium, proved to be a good alternative for improving the efficiency and the fill factor of vegetal pigments based DSSCs.

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