

Potential of Betanin Natural Dye for Solar Cells Application

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Research article

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Abstract

Background: A photovoltaic cell, or solar cell, is an electronic component which, exposed to light, produces electricity thanks to the photovoltaic effect. Organic photovoltaic cells are photovoltaic cells of which at least the active layer consists of organic molecules. It has a yield of at least 15%. The future prospects of the research for solar cells application has required for the development in the field.

Main body: Dye-sensitized solar cells are considered to be promising candidates for low-cost solar energy harvesting using sustainable and environmentally friendly materials. In general, solar cells sensitized to dyes consist of three parts: TiO₂ sensitized to the photoanode dye with porous film on a transparent conductive glass, an electrolyte solution penetrating through the TiO₂ anode film, and the conductive oxide transparent platinum glass as counter electrode.

Conclusion: In this work, betanin dye was extracted from mature red fruits of *Opuntia ficus indica* and purified with fractional crystallization protocol using an 8:2 (v/v) ratio of ethyl acetate/ethanol. TiO₂-films with different thickness values have been prepared CV and US sensitization of TiO₂-films using betanin dye prove an enhancement on the uniformity distribution of the dye on the film in case of US method. Emission spectra of Dye-TiO₂ films have been measured and show a hyperchromic shift of the emission intensity with the increase of the thickness due to the augmentation of betanin content. A comparison between the photovoltaic properties of prepared betanin_DSSC and N719 dye_DSSC reveals that betanin dye could be successfully proposed as a sensitizing dye in solar cell applications.

Introduction

Since the end of the 20th century, energy has been at the heart of all debates and has finally proved to be one of the major challenges facing developed societies. Indeed, the vast majority of global energy consumption is provided by the exploitation of non-renewable fossil resources, such as oil, gas and even coal [1–3].

However, although still abundant at present, the inevitable depletion of this type of resource poses, due to the growing world energy demand, important questions concerning the guarantee of access to energy for future generations. In this context, renewable energies, such as wind, geothermal, hydroelectric or solar, are today the subject of a major research effort [4–6]. Among these energies, photovoltaics, consisting of the direct conversion of solar energy into electricity, have experienced significant growth in recent years, with energy efficiencies of the order of 15 to 18% for the modules currently marketed [7]. This energy could therefore represent in the short term a viable alternative to fossil fuels. However, much progress remains to be made in this area. Among the new concepts studied, solar cells sensitized with natural dyes constitute a promising technology for the replacement of conventional solar cells and have given rise to a great deal of research since the first work established by Grätzel et al. in 1991 [8]. One of the main areas of research in the field is the development of new photosensitizers to increase the collection of sunlight. Betalains were known as natural dyes with high extinction coefficient values and have attracted the

interest of many researchers due to their properties [9, 10]. In this context, we propose in this paper to study the potential of purified betanin dye on the DSSC applications.

Experimental Procedure

Extraction of natural dye sensitizers

Mature red fruits of *Opuntia ficus-indica* were macerated in a blender. Directly, the resulted juice was subjected to the dye extraction process. 50 g of the obtained juice was mixed with 100 mL of an extraction solvent. To optimize the extraction process, eight different extraction solvents with different polarity properties have been tested, corresponding to distilled water, ethanol, acetone, methanol, chloroform, ethyl acetate, toluene and dichloromethane (DCM). Extraction was elaborated under sonication conditions (25 kHz, 100 W) for 15 minutes [11]. After extraction, the filtrate was recovered by simple filtration through a filter paper on a Büchner funnel. Filtrate was evaporated in vacuum at 40 °C and the concentrate was kept in dark to prevent any degradation.

Isolation and NMR characterization of the extracted dye

The concentrated extract kept on the Sect. 2.1, was subjected to a fractional crystallization protocol using a 8:2 (v/v) ratio of ethyl acetate/ethanol. The recovered solid was subjected to NMR analysis using a Bruker AC 600 spectrometer. Chemical shifts are given in parts per million relatives to tetramethylsilane (TMS) and the coupling constants J are given in Hertz. The spectrum was recorded in CD₃OD as solvents at room temperature.

Preparation of Dye-TiO₂ films as a photoanode

In order to ensure the optimal efficiency of the prepared material, anatase TiO₂ nano-powder of an average particle size about 21 nm was supplied by Sigma-Aldrich [12, 13]. Various films of TiO₂ with different thickness were prepared referring to doctor blade method on a FTO glass substrate and heated at 450 °C for 1 h [14]. The sensitization was conducted conventionally (CV) by soaking the prepared films into a saturated aqueous dye solution for 24 hours and using ultrasound (US) by soaking the prepared films into a similar dye solution for 1 hour at a frequency of 25 kHz and a power about 100 W.

Finally, in order to eliminate any unattached dye from the surface of the film, the sensitizer films were rinsed with ethanol.

Preparation of the cathode

In order to prepare Platinum_FTO cathode, a solution of H₂PtCl₆ in isopropanol (7 mM) was placed on the FTO glass and kept till spread homogenously on the surface and then dried at ambient atmosphere. Dried Pt_FTO glass was then heated at 450°C for 30 minutes [15].

Cathode and photo anode were then coupled by binding clips and Iodide electrolyte solution were injected into the cell.

Characterization and measurements

UV–vis-NIR spectrometer (Shimadzu UV-3600) was used to plot the ultraviolet-visible (UV–vis) absorption spectra of the extracted dye with different extraction solvent and to register the diffuse reflectance spectra before and after natural dye loading on TiO₂ films for 24 hours in case of conventional sensitization and 1 h in case of ultrasonic sensitization.

In order to appraise the effect of the thickness value of TiO₂ films on the sensitization results and also on the photovoltaic properties of the prepared materials, 1 cm² of Dye-TiO₂ films with different thickness values were immersed in 7.5 mL of 1 mM KOH aqueous solution to measure the desorption of the dye from the TiO₂ films [16]. The quantification of the desorbed betanin dye (BC) was calculated based on the following equation [17]:

$$\text{BC [mg/L]} = [(A \times \text{DF} \times \text{MW} \times 1000 / \epsilon \times L)]$$

where A is the absorption value at the absorption maximum, DF is the dilution factor and L is the path-length (1 cm) of the cuvette. The molecular weight (MW) and molar extinction coefficient (ϵ) of betanin, were {MW = 550 g/mol; ϵ = 60,000 L/(mol cm) }.

The color difference (ΔE) measurements for the Dye-TiO₂ films were evaluated by light reflectance measurements using SF 300 spectrophotometer.

The fluorescence spectra for the Dye-TiO₂ films with different thickness values were measured using Perkin-Elmer LS-3 Fluorescence Spectrophotometer coupled to an excitation source (Xenon lamp, 150W) at a wavelength of 350 nm.

Scanning electron microscope (Jeol Model 6360 LVSEM) was used to study the morphology of TiO₂ films and sensitized TiO₂ film samples.

Results

Effect of the extraction solvent on the extraction efficiency of natural dye sensitizers

This section has been developed in order to select the most efficient solvent on the extraction of betacyanin dyes. The uv-visible absorption spectra of the extracted dye with the selected solvents are exposed in Fig. 1. As the spectra demonstrate, the selected extraction solvents are divided according to their polarity on two categories. The first category is attributed to the solvents with high polarity (water, ethanol, acetone and methanol); all the visible absorption spectra of this category present a maximum of absorbance around 538 nm corresponding to betanin dye [18, 19], the maximum of absorbance was

registered in case of ethanolic extract. The other solvents with moderate to low polarity fail to solvate betacyanin dyes and the obtained spectra did not present any remarkable peak.

¹H NMR study of the purified extracted dye

Table 1 shows the attribution of protons, chemical shifts and couplings constants of protons in betanin.

Table 1
Chemical shifts and couplings constants of betanin

Chemical shifts (ppm)	Integration, multiplicity, coupling constant (Hz)
8.29	1H, d, $J_{H10-H11} = 12.0$ Hz, H-10
7.19	1H, s, H-7
7.15	1H, s, H-4
6.43	1H, s, H-17
6.36	1H, d, $J_{H11-H10} = 12.0$ Hz, H-11
4.93	1H, H-1'
4.73	1H, dd, $J_{H14-H13a} = 7.0$, $J_{H14-H13b} = 5.6$, H-14
4.65	1H, t, $J_{H2-H3} = 7$ Hz, H-2a
4.28	1H, dd, $J_{H6'a-H5'} = 2.0$ Hz, $J_{H6'a-H6'b} = 12.0$ Hz, H-6'a
4.15	1H, dd, $J_{H6'b-H5'} = 5.3$ Hz, $J_{H6'b-H6'a} = 12.0$ Hz, H-6'b
3.95–3.83	3H, m, H-2', H-13a, H-5'
3.71–3.84	4H, m, H-3, H-13b H-3', H-4'

Quantification of the desorbed betanin dye through Dye-TiO₂ films with different thickness values under CV and US sensitizing method

Sensitizing dyes are known to bigly alter the photovoltaic parameters of a DSSC [20, 21]. So, in this section we summarize the quantification results of betanin dye in Dye_TiO₂ films prepared in different thickness values under CV and US sensitizing method. As Fig. 3 shows, the amount of the desorbed dye through the Dye_TiO₂ film, under CV and US sensitizing method, increase proportionally with the thickness of the film. It was also noted that the amount of the dye absorbed through the film is approximately the same for the two adopted sensitizing method in case of a same studied thickness of a film.

Spectral Study of the dispersion uniformity of betanin dye on the TiO₂ films under CV and US sensitizing method

The uniform distribution of the sensitizing dye through the DSSC film is an important parameter to study [22]. In order to investigate the betanin dye distribution through the prepared films, we opted here to measure the color difference ΔE at equidistant points in the prepared Dye_TiO₂ films sensitized under CV and US method. Results are summarized in Fig. 4. As Shown from the data, all the ΔE measurements are below the value 1.

Optical property of Dye_TiO₂ films: Fluorescence measurements

Fluorescence properties of substances are extremely related to their photoelectron emission character which could correlate with the photoelectric conversion property. Figure 5 summarizes the emission spectra of Dye_TiO₂ films with different thickness values [23].

It was observed for all the studied samples of Dye_TiO₂ films with different thickness values that the maximum of emission intensity was registered around 650 nm.

Morphologic study of TiO₂ films and Dye_TiO₂ films

In order to investigate the influence of the sensitization on the morphology of the prepared films, SEM analysis have been established for TiO₂ film (Fig. 6-a) and Dye_TiO₂ films (Fig. 6-b). As Fig. 6-a shown, the manual application of TiO₂ generates an unequal distribution on the surface of the film. Any significant modification has been detected on the SEM image of the Dye_TiO₂ film (Fig. 6-b). Both Fig. 6-a and Fig. 6-b present a highly porous shape.

Photovoltaic properties of betanin sensitized solar cell: Comparative study with N719 dye sensitized solar cell

N719 dye has been previously used as a common sensitizing dye in DSSC applications [24]. In this section, a comparative study on the photovoltaic properties between betanin sensitized solar cell and N719 dye sensitized solar cell has been developed. Current-voltage (J-V) measurements have been made under the 100 mW/cm² (AM 1.5). Results are summarized in Fig. 7.

As seen on the figure, the values of J and Voc measurements, for each studied thickness value of TiO₂_film, are too near in case of betanin_DSSC and N719 dye_DSSC.

for TiO₂_films with different thickness values

Discussion

The maximum of absorbance was registered in case of ethanolic extract. The structure of betanin is confirmed by ¹H NMR proton spectra. The prepared films seem uniform to the human eye. Whereas, it is

clearly shown that for all the studied Dye_TiO₂ films, the ultrasonic sensitization leads to a better distribution of the dye through the film since the entire ΔE measurements are below 0.3. The most uniform distribution of the dye in case of US sensitization method could be attributed to the sono-capacity to prevent the aggregation phenomena of the dye [25]. US_Dye_TiO₂ films were chosen to develop the following sections. SEM analyses have been established for TiO₂ film before and after sensitization in order to control the influence of the sensitization on the morphology of the films. Generally the thickness values of the prepared TiO₂_films affect enormously the performance of the DSSC. Indeed, the J measurements increase from 11.1 to 14.1 (mA/cm²) in case of the prepared betanin_DSSC. The increase of the thickness value of dye_TiO₂ films induces a hyperchromic shift of the emission intensity. The obtained result could be attributed to the greater amount of betanin content in the thicker Dye_TiO₂ films, as deduced in the Sect. 3.3.

These results could be attributed to the higher amount of sensitizing dye present in the thicker TiO₂_film as verified in the Sect. 3.3 of this paper. This leads that betanin dye could be successfully proposed as a sensitizing dye in solar cell applications.

Conclusion

Betanin sensitizing dye was extracted from mature red fruits of *Opuntia Ficus indica*. An optimization of the extraction study has been monitored through using different extraction solvents and the optimum extraction solvent was ethanol. Betanin dye was purified using fractional crystallization protocol and characterized by ¹H NMR spectroscopy. Different thickness of TiO₂_films were prepared and subjected to CV and US sensitization process using betanin dye.

The quantification of the desorbed betanin dye through Dye_TiO₂ films reveals that the betanin content increase proportionally with the thickness of the film and are approximately the same for each thickness for the two sensitization methods. Whereas, the study of the uniformity distribution of the dye on the film show an enhancement in case of US sensitization method. Also, the emission spectra of Dye_TiO₂ films with different thickness values have been measured and it was shown that the increase of the thickness value induce a hyperchromic shift of the emission intensity centered at 650 nm.

A comparative study of the photovoltaic properties of prepared betanin_DSSC and N719 dye_DSSC reveals that betanin dye could be successfully proposed as a sensitizing dye in solar cell applications.

Declarations

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Availability of data and materials

Not applicable.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Figures

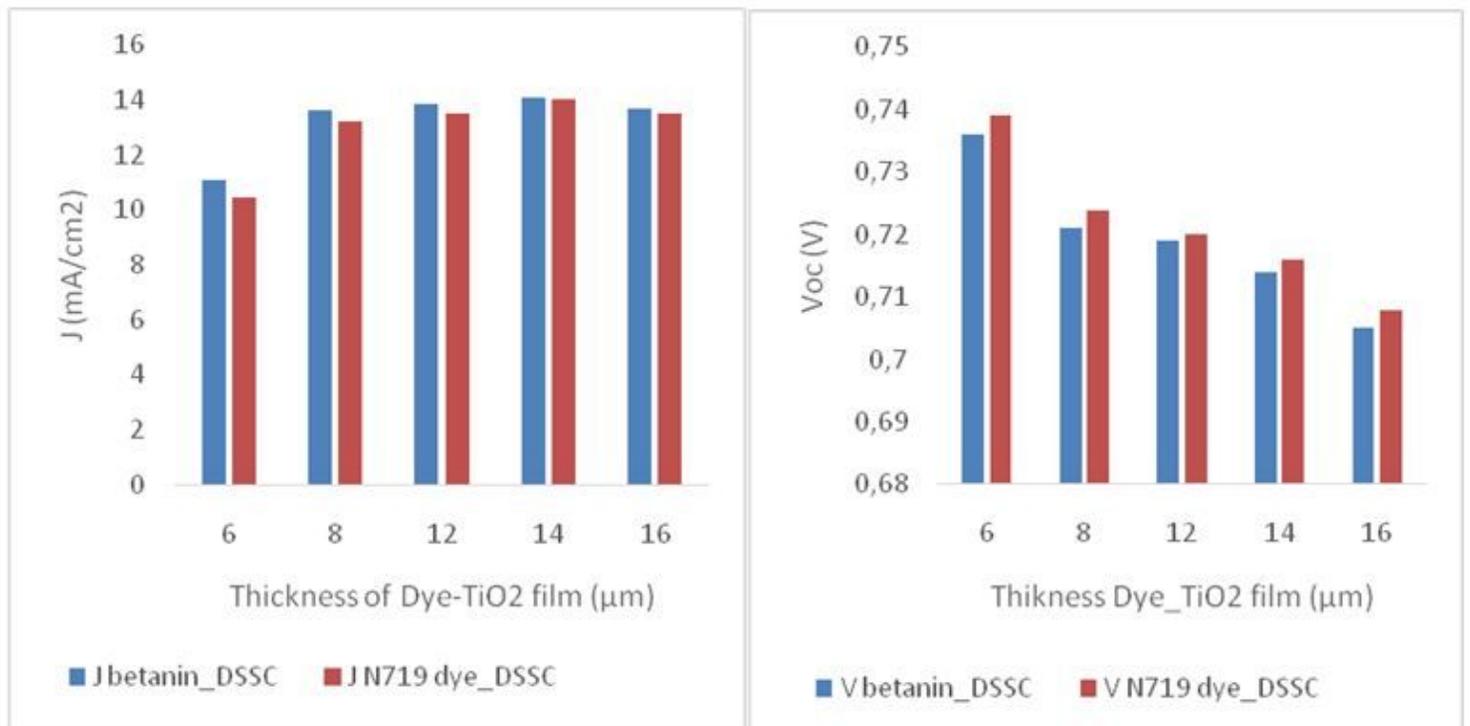


Figure 1

J and V measurements of betanin_DSSC and N719 dye_DSSC for TiO₂_films with different thickness values.

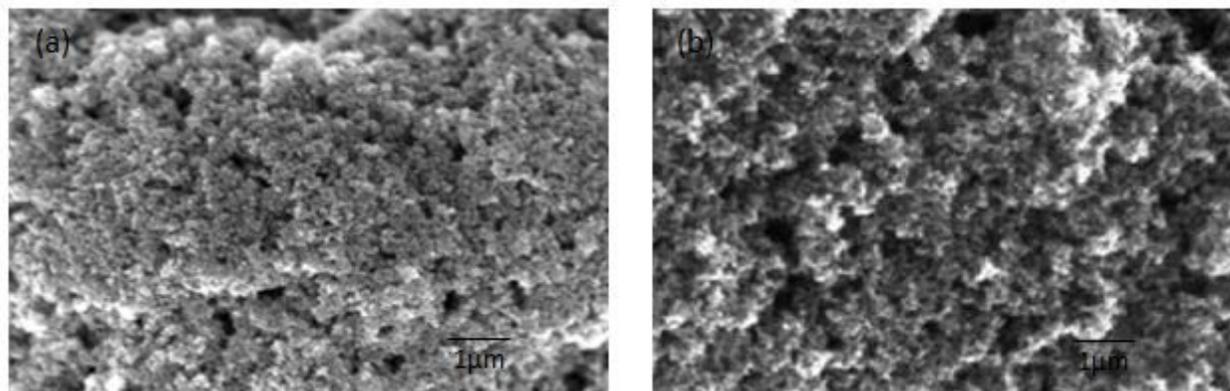


Figure 2

SEM images of TiO₂ films (a) and Dye_TiO₂ films (b).

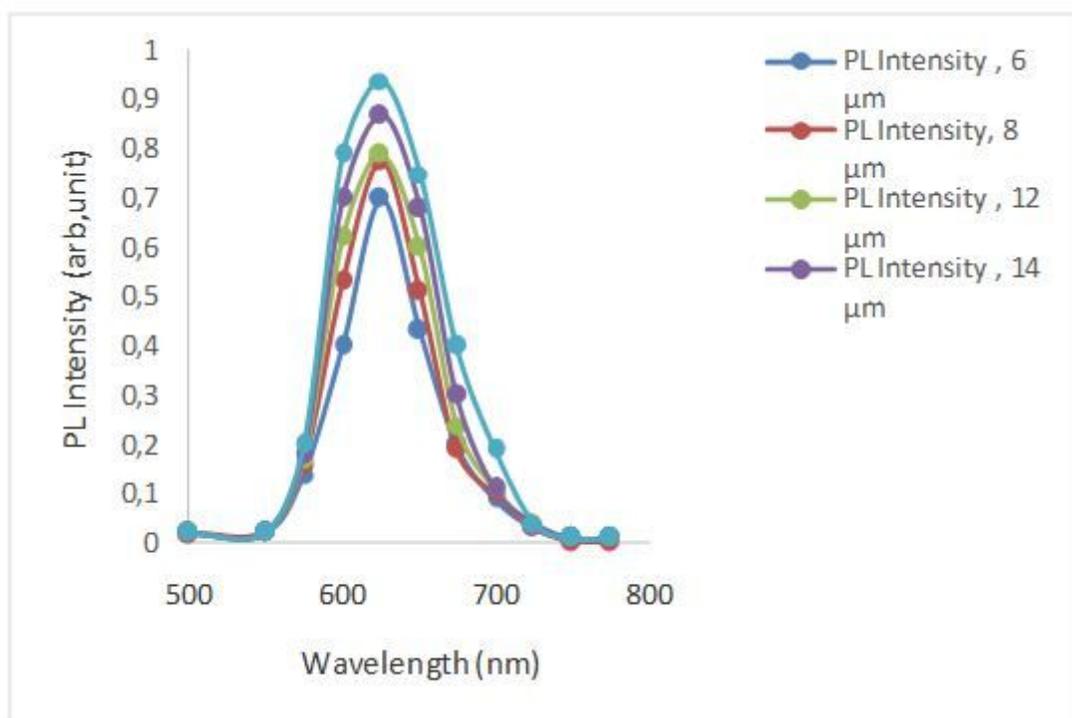


Figure 3

Emission spectra of Dye-TiO₂ films with different thickness values, (λ excitation = 350 nm).

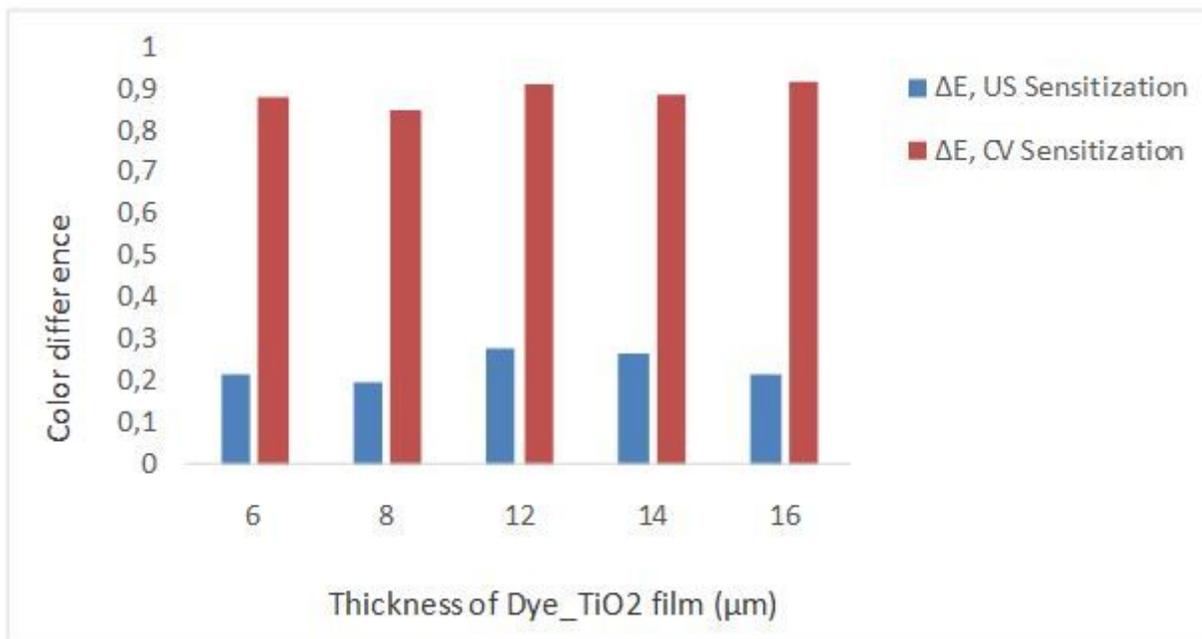


Figure 4

ΔE measurements on Dye_TiO2 films sensitized under CV and US method.

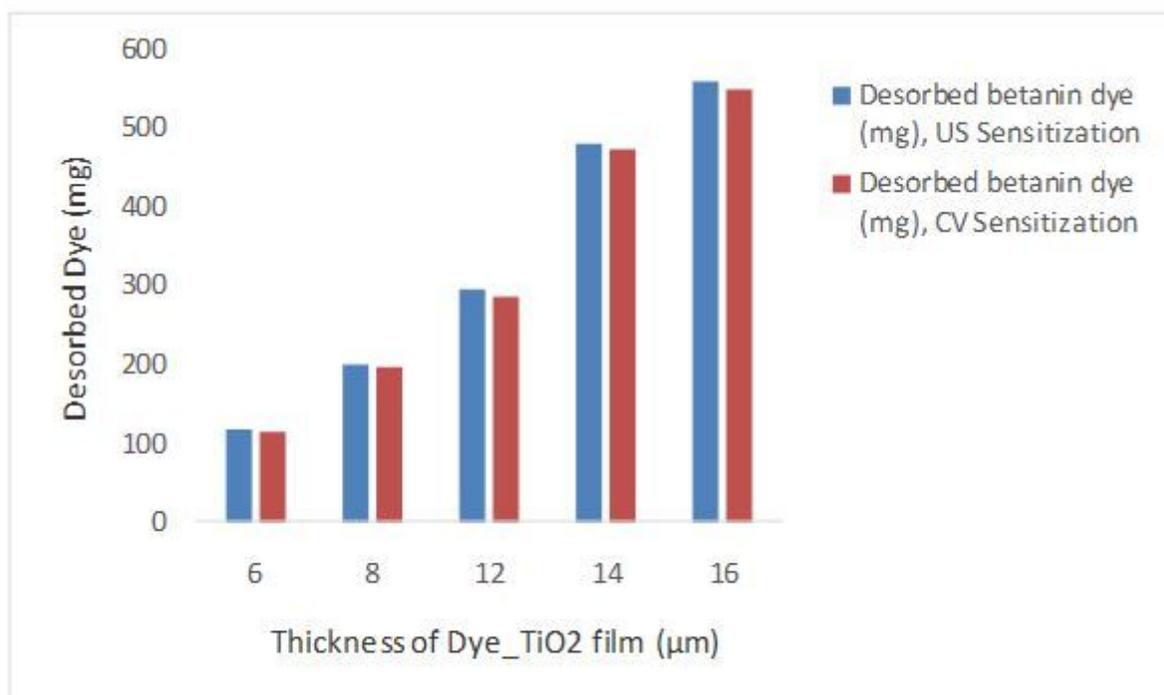


Figure 5

Quantification of the desorbed betanin dye.

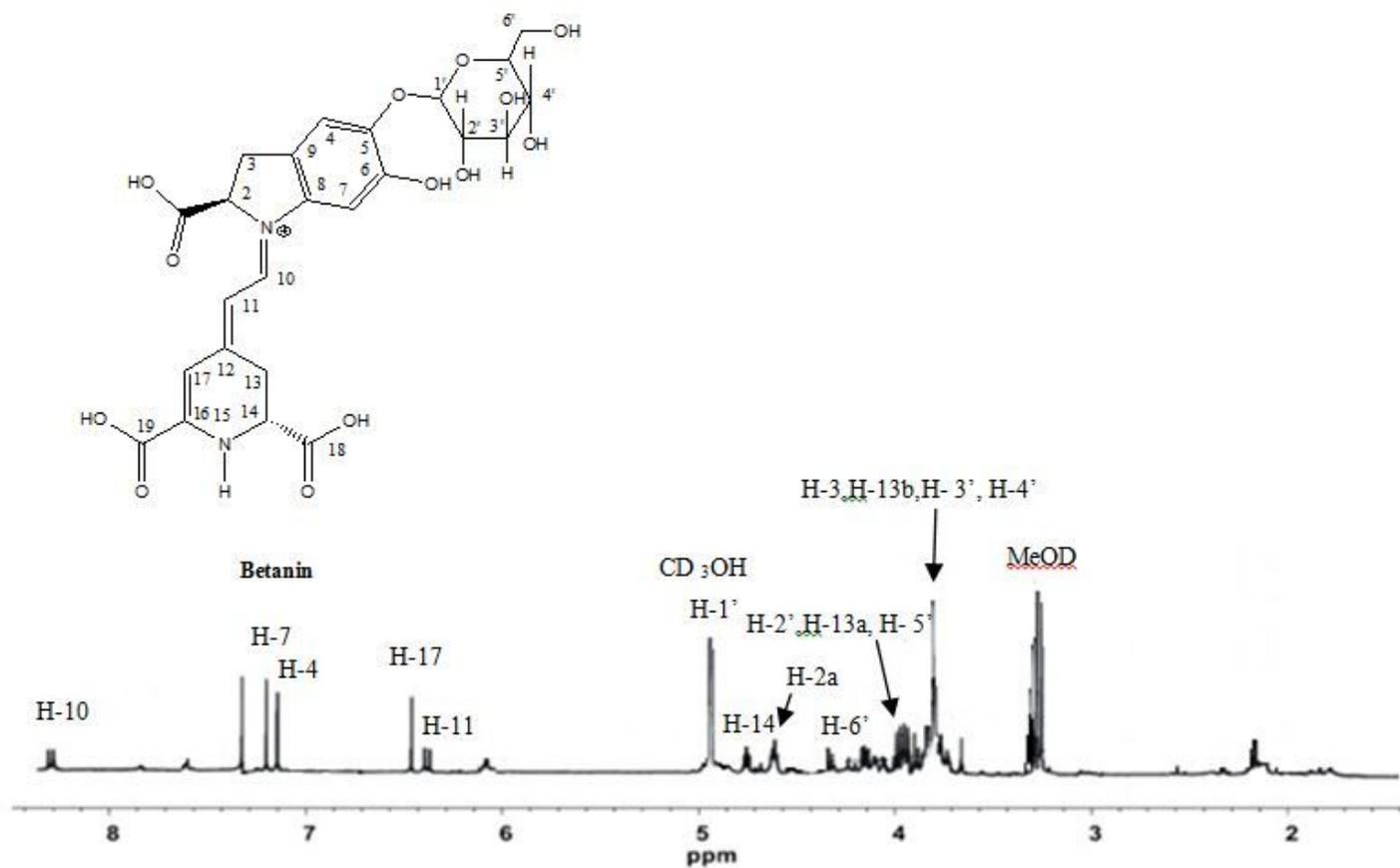


Figure 6

¹H NMR proton of betanin in CD₃OD.

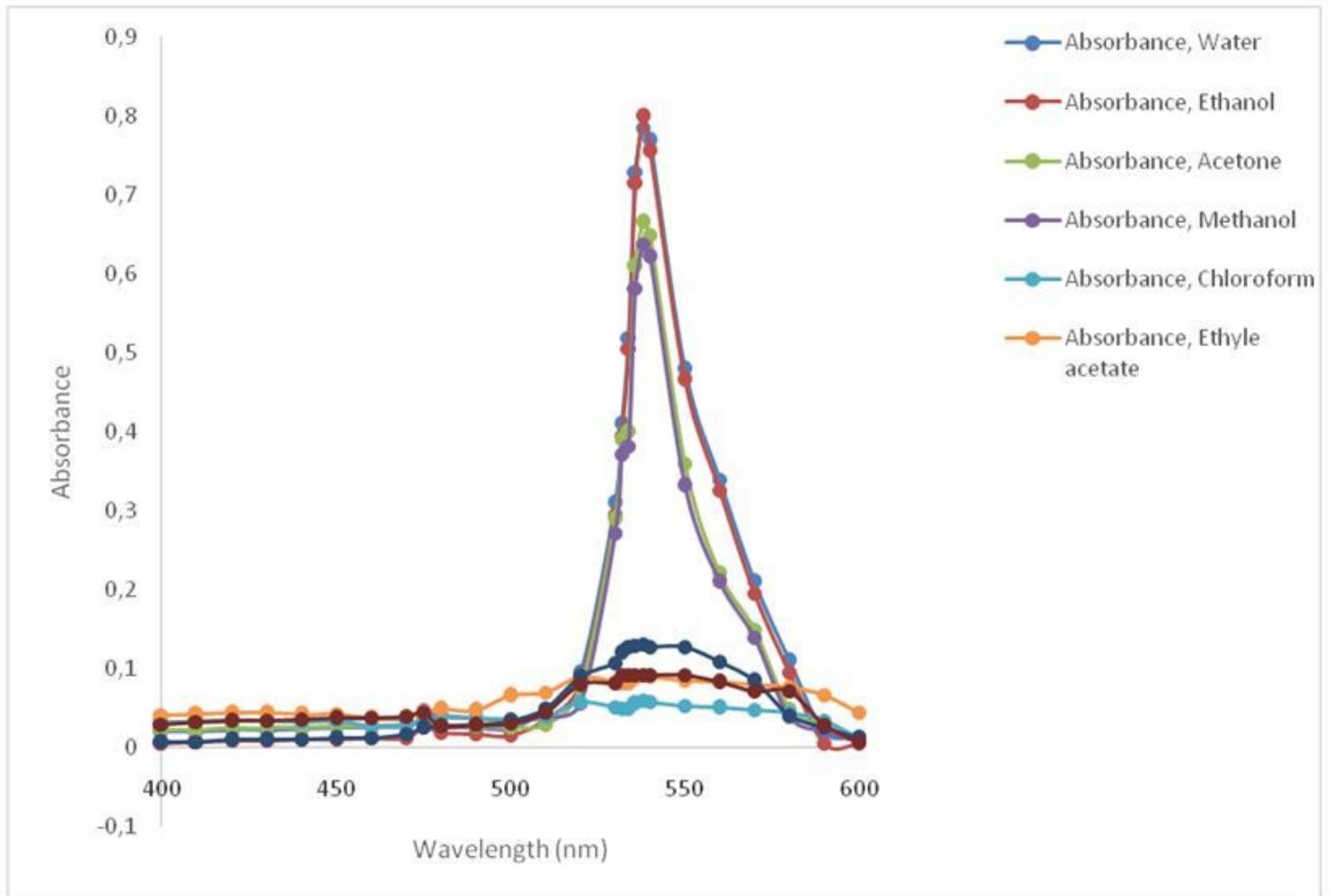


Figure 7

Visible light absorption spectra of the extract obtained in different extraction solvent.