Study of *Beta vulgaris* (Beetroot) Extraction in Polar Solvents as Photoabsorber in Dye-Sensitized Solar Cells Application

Norfatihah Mohd Adenam¹, Nur Alfarina Pirdaus¹, Muhamad Yuzaini Azrai Mat Yunin¹, Ku Azmie¹, Khairul Nizar Syazwan Wan Salihin Wong³, Hasyiya Karimah Adli¹,²*, Hasiah Salleh³

¹Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia.
²Institute for Artificial Intelligence and Big Data, Universiti Malaysia Kelantan, 16100 Kota Bharu Kelantan, Malaysia.
³Centre for Fundamental and Liberal Education, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

E-mail: hasyiya@umk.edu.my

Abstract. Over the last two centuries, energy needs have increased substantially until non-renewable resources nearly come to depletion. Therefore, the application of renewable energy resources like solar energy is absolutely appointed favorable due to its economical impact and improved technology. Dye-sensitized solar cell (DSSC) being the type of solar cell that utilize dye as light sensitizer for the operation and become the best alternative rather than toxic chemical dyes. Betalains is one of the pigment of natural dyes that can be extracted from fruit and vegetables which majorly available in beetroot (*Beta vulgaris*). To get the pigment for solar cell application, the optimum extraction is crucial. Hence, in this study, several polar solvents such as distilled water, methanol, ethanol, isopropanol, n-butanol, formic acid and acetic acid were used to extract betalain pigment from *Beta vulgaris* (BV). Then, several characterizations were carried out to analyze the photoabsorber properties using Ultraviolet-visible Spectroscopy (UV-Vis), Fourier-Transform Infrared Spectroscopy (FTIR), High Performance Liquid Chromatography (HPLC) and Scanning Electron Microscopy (SEM). The energy bandgap of BV in different solvents (ITO/TiO₂/BV) are 2.19, 2.35, 2.65, 2.73, 2.78, 2.98 and 3.00 eV for methanol, n-butanol, formic acid, ethanol, acetic acid, water and isopropanol respectively. Whilst, FTIR spectrum shows the presence of functional group of O-H, C=O and C-O-C and HPLC analysis depicted the existence of betacyanin pigment all in samples. SEM images show the presence of porous structure of TiO₂ and irregular pits formed due to the formation of BV layer on TiO₂. In conclusion, overall findings suggested that methanol is the best solvent for extraction of betalain pigment, answering it has best photoabsorber properties among the sample series. Further detailed study is recommended to maximise the potential of *Beta vulgaris* pigment as photoabsorber in DSSC application.

1. Introduction

Since last two centuries, energy needs increased substantially until non-renewable resources such as fossil fuel, coal and natural gas nearly come to depletion [1]. Thus, the application of renewable energy resources such as solar energy technology has been explored and utilized. Meanwhile, dye-sensitized solar cells (DSSCs) are the most economical type of solar cell that easy to fabricate and environmental-friendly. DSSCs is made up of a sandwich-like structure that consists of natural dyes as light sensitizer
anode or also known as photoabsorber and electrolyte, as illustrated in Fig. 1. The utilization of natural dye is the best alternative to avoid environmental issues regarding toxicity of chemical dyes [2,3].

![Figure 1. Structure of DSSC](image)

Betalains is common pigment extracted from fruits and vegetables which major available in beetroot (*Beta vulgaris*) based on widely reported [4]. Few solvents have been used by previous researcher for the extraction of *Beta vulgaris* such as citric acid, ethanol, methanol and ascorbic acid [5-7]. Hence, the optimum extraction of these pigments is crucial in order to ensure high quality of photoabsorber properties. Thus, the choice of polar solvents towards high extraction yields was the ultimate objective of this study. The series of polar solvents such as water, methanol, ethanol, isopropanol, n-butanol, formic acid and acetic acid were used to extract betalains pigment from *Beta vulgaris* to identify the best solvent for extraction of the red-violet colour, which indicate the presence of betacyanin pigment.

2. Experimental Method

2.1. *Beta vulgaris* Extraction

About 14 g of *Beta vulgaris* (beetroot), BV peels were rinsed with distilled water and subsequently were cut into small pieces, grinded before dissolving into formic acid, n-butanol, acetic acid, distilled water, methanol, isopropanol and ethanol denoted as A, B, C, D, E, F and G respectively. The solutions were kept stirring and heating for 45 minutes at room temperature. Later, the dyes solutions were stored overnight at 4°C under dark condition before filtered and centrifuged. The final solution were kept overnight before further use.

2.2. TiO$_2$/BV Thin Film Fabrication

Titanium Dioxide (TiO$_2$) paste was prepared by dissolving about 2.0 g of TiO$_2$ nanoparticles into 100 ml of ethylene glycol and ethanol until homogeneous paste was obtained. Later, 1 ml of the prepared TiO$_2$ paste was mixed with 100 ml of ethanol. TiO$_2$ paste solution was room placed under dark condition and ready for the preparation of TiO$_2$ thin film by using doctor blade technique. These TiO$_2$/ITO glass was sintered at 500°C for 30 minutes ramp time, then dyed with BV extracts for overnight at room temperature.

2.3. Characterization

The absorption spectra of BV and TiO$_2$/BV thin films were determined using UV-Vis spectrophotometer in the wavelength range of 400 nm to 800 nm. From the absorption spectra, the bandgap energy of dye was evaluated using Tauc-plot method. Hence, the spectral properties and the functional group of *Beta vulgaris* (beetroot) dyes were detected using Fourier Transform Infrared Spectroscopy (FTIR) (Thermo ScientificTM iD7) with single bounce attenuated total reflectance (ATR) technique in scan range of 400 cm$^{-1}$ until 4000 cm$^{-1}$. The chemical compounds present was analyzed by High Performance Liquid Chromatography (HPLC) (Shimadzu SPD-M20A) using two mobile phase which are Solvent A (1.5%
phosphoric acid in water) and Solvent B (1.5% phosphoric acid, 20% acetic acid, 25% acetonitrile in water) with flow rate of 0.7 mL/min, injection of 20µL with detection at 540 nm for 30 minutes. The surface morphology of TiO$_2$/BV was observed by using Scanning Electron Microscope (SEM) at 1000× of magnification.

3. Result & Discussion

3.1 Physical Observation

From physical observation on the colour of *Beta vulgaris* (beetroot) dye solutions (Figure 2), BV dyes methanolic solutions retained its concentrated red-violet colour even after 1 week. The solubility of betalain pigment from *Beta vulgaris* in the tested solvents can be arranged in the sequence of methanol (E) > ethanol (G) > water (D) > formic acid (A) > acetic acid (C) > isopropanol (F) > n-butanol (B) based on the physical observation of their colour intensity. Thus, it can be said that the extraction of betalains might be successfully performed in methanolic solvents [8].

![Figure 2. Final colours of BV extracts.](image)

3.2 UV-Vis Analysis

From UV-vis spectra, all extracts formed a broad range of absorption between 450 and 540 nm, almost similar previously reported [9]. In the visible region, the absorbance spectra of BV extract for protic polar solvent eg., water, ethanol, and methanol show broad peak at around 500 to 560 nm, due to presence of red-violet betacyanins dye. It was reported that betalains have strong absorption between 400–600 nm range due to the color combination of yellow–orange betaxanthins and red–violet betacyanins [10]. Figure 3 shows the UV-Vis spectra of BV in all solvents.

![Figure 3. UV-vis Spectra of Beta vulgaris dyes in different solvents.](image)

Meanwhile, Figure 4 shows the absorption spectra of ITO/TiO$_2$/BV with maximum peak appeared at around 500 nm to 600 nm for all types of solvents used. The absorption of ITO/TiO$_2$/BV exhibit broad
peaks and blue-shifted suggesting the betanin pigment on TiO$_2$ was formed. Besides, the absorption spectra indicated the interaction of betalain dye molecules with TiO$_2$, to produce an ester-type linkage and boost electrons from the lowest unoccupied molecular orbital (LUMO) of the dye to the conduction band of TiO$_2$ to facilitate rapid electron transfer by coupling effect [11-13].

![Figure 4. UV-vis Spectra of ITO/TiO$_2$/BV in different solvents.](image)

### 3.3 Fourier-Transform Infrared Spectroscopy

Fig. 5 shows all spectrum of BV in different solvents with different absorption bands characteristics of functional groups of betalain. From the spectra, all solutions except that in acetic acid and formic acid have shown a strong and broad band from 3200 to 3500 cm$^{-1}$ that belong to the -OH group. The peak at 2950 cm$^{-1}$ represents to $\delta$-CH stretching vibration because of the existence of aromatic -CH group in extracted dye. The bending vibration observed at 1700 cm$^{-1}$ was assigned to the carbonyl group (C=O) in betacyanin. Due to the presence of C=C aromatic ring stretching vibrations, a strong stretching vibration was also observed at 1622 cm$^{-1}$. Other than that, the peak at 1053 cm$^{-1}$ is referred to the C-O-C stretching vibrational modes of acid and carbohydrate groups. Within the spectral region, the main vibrational characteristics associated with carbonyl compounds of the betanin molecule also was observed. The initial decarboxylation site of betacyanin might depend on the type of solvent [14]. Overall FTIR spectra obtained justifying the presence of betacyanin pigment that proven by the presence of hydroxyl group and double bound aromatic ring.

![Figure 5. FTIR Spectra of Beta vulgaris in different solvents.](image)
3.4 High Performance Liquid Chromatography Analysis

The presence of betalain compound in *Beta vulgaris* dyes prepared was determined using HPLC chromatogram at 540 nm. The highest peak with retention time of 3.6 min was observed for all seven types of solvent for beetroot dyes. This finding can relate that all dyes have the same compound, indicated the presence of betalain compound or red-violet betacyanin pigment.

![HPLC Chromatogram of Beta vulgaris dyes in different solvents.](image)

**Figure 6.** HPLC Chromatogram of *Beta vulgaris* dyes in different solvents.

From Figure 6, three peaks were observed at 535 nm which corresponding to betanin, betanidin, and isobetanin [15]. The identification of betalains can be deduced from its chromatographic behavior and proven through analysis of its absorption spectrum and retention time [15].
3.5 Scanning Electron Microscopic

Figure 7 shows the surface morphology of each prepared-extracts solutions (A-G) doped on TiO\textsubscript{2}. It can be seen that the typical porous structures of TiO\textsubscript{2} were found for all samples, with some irregular size of pits present. This can be explained due to the doping of dyes on TiO\textsubscript{2} that finally formed thick compact layer covers the whole TiO\textsubscript{2} surface without agglomerations of particles was observed. The presence of holes of TiO\textsubscript{2} is acting as spots for an extensive penetration of the dye molecules [16,17]. These highly porous layers with large surface areas are readily available to dyes for rapid adsorption and favourable for solar cells application. The smooth porous structure of surface morphology of ITO/dyes can elevate short circuit current density that result the enhancement of electrochemical performance [18].

![SEM images of ITO/TiO\textsubscript{2}/BV dyes extracted in different solvents of A-G which are formic acid, n-butanol, acetic acid, distilled water, methanol, isopropanol and ethanol respectively.](image)

3.6 Band gap Measurement

The Tauc plot was derived from UV-vis spectra of ITO/TiO\textsubscript{2}/BV at 540 nm and the estimation of the optical band gap value was made based on the intersection of the dashed line with the x-axis of energy (eV), with the formula shown in Table 1. The Tauc optical gap is determined through an extrapolation of the linear trend observed in the spectral dependence of (\(\alpha h\nu\))\(^{1/2}\) over a limited range of photon energies \(h\nu\).

| Band Gap Energy (E) = hc/λ |
|--------------------------|
| Planck constant (h) = 6.63 x 10\(^{-34}\) Joules sec (J.s) |
| Speed of light (C) = 3.00 x 10\(^8\) meter/sec (m/s) |
| Cut off wavelength (λ) = *obtained from UV-vis absorbance spectrum in meters |

| h  | C   | λ   | E   | eV  |
|----|-----|-----|-----|-----|
| 6.63x10\(^{-34}\) | 3.00x10\(^8\) | From UV-Vis | From calculation | From calculation |

Where 1 eV = 1.6 x 10\(^{-19}\) Joules (conversion factor)

The band gap energy values of BV/ TiO\textsubscript{2} in different solvents calculated as following 2.19, 2.35, 2.65, 2.73, 2.78, 2.98 and 3.00 eV from solvents of methanol, n-butanol, formic acid, ethanol, acetic acid, water and isopropanol respectively. From the result, BV in methanolic solvent recorded the lowest band gap (2.19 eV). The lowest bandgap value was said here an energetic driving force for the electron and hole separation [19]. Thus, electrons have energetically favoured to travel from the dye to the semiconductor band. The dye later get oxidised and positive charge was obtained [20]. Therefore, the lowest energy bandgap was favorable in order to get oxidized faster and get higher conductivity [21].
Conclusion
From the overall findings, it can be concluded that the best solvent for the pigment extraction of *Beta vulgaris* is methanol, evaluated through UV-vis absorption analysis and lowest energy bandgap (2.19 eV) in which can provide higher conductivity values. The optimization on the dye extraction can produce the best photo absorber properties with lowest bandgap value that can indicate higher potential in DSSCs application.

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