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S. Suhaimi, N. M. Nasri, S. Wahab, N. S. Ismail, M. M. Shahimin, and Z. Sauli

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Ultraviolet-Visible Absorbance Analysis on Solvent Dependent Effect of Tropical Plant Anthocyanin Extraction for Dye-Sensitized Solar Cells

S. Suhaimi[1, 2, a)], N. M. Nasri[1], S. Wahab[1], N.S. Ismail[1, b)], M.M. Shahimin[3, c)]
and Z. Sauli[4]

[1] *School of Microelectronic Engineering, Universiti Malaysia Perlis (UniMAP),*
Pauh Putra Campus, 02600 Arau, Perlis, Malaysia.

[2]*Faculty of Engineering Technology (FTK), Universiti Malaysia Perlis (UniMAP),*
Aras 1, Blok S2, UniCITI Alam Campus, Sungai Chuchuh, Padang Besar, 02100 Perlis, Malaysia

[3]*Department of Electrical and Electronic Engineering, Faculty of Engineering,*
National Defence University of Malaysia (UPNM), Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia.

[4]*Universiti Malaysia Kelantan, Jeli Campus, Locked Bag 100, 17600 Jeli, Kelantan, Malaysia.*

[a)]Corresponding author: suriatisuhaimi89@gmail.com
[b)]syakimah@unimap.edu.my
[c)]mukhzeer@upnm.edu.my

Abstract. In the current investigation, natural tropical dyes extracted from Mulberry, Roselle and Oxalis Triangularis were used as natural dye sensitiser. Four different extraction solvents, namely acetone, ethanol, a mixture of acetone and ethanol (v/v 1:2) and distilled water were employed to extract natural anthocyanin dyes from Mulberry, Roselle and Oxalis Triangularis. The natural dye extraction process was analysed using ultraviolet-visible spectroscopy, and the spectrum was taken in the wavelength range of 400 nm to 800 nm. The main photoactive component of Mulberry, Roselle and Oxalis Triangularis are anthocyanins compound which considered as an unstable pigment that undergo gradual degradation processes throughout storage or use. The spectra can be seen, that there are differences in its intensity where ethanol and acetone solvent was much higher absorbance peak vis-à-vis the other solvents. Mulberry and Roselle extraction in ethanol shows the high absorbance intensity at wavelength 550 nm, while Oxalis Triangularis extraction in acetone shows the higher absorbance at the peak of 664 nm. This indicates the presence of more anthocyanins compound that absorbs a higher number of photon energy light source. It is also appears that the dye extraction performance gradually degrade after seven days storage in dark condition. Mulberry and Oxalis Triangularis extraction in mixture of acetone and ethanol exhibit low degradation percentage about, 0% and 32%, respectively, while Roselle extraction in DI water reveal 0% degradation after 7 days.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been considered as an attractive alternatives for photoelectrochemical conversion of visible light into electricity due to the low manufacturing cost, flexible substrate, light weight, and abundant availability of fabrication materials. DSSCs are based on a thin nanoporous film of semiconductor, titanium dioxide (TiO_2) also known as titania which provides a high surface area for adsorption of the dye [1-2]. In the assembly of DSSCs, dye plays an important role in harvesting solar energy and converting to electrical energy with the aid of semiconducting photoanode [3]. Considering its function, dye sensitiser is indeed one of the important components playing important role to enhance the DSSCs performance in which it absorbs light spectrum and function as an anchoring chemical group to improve electron injection conduction band of TiO_2 [4]. Thus, researchers have much

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interests in introducing new families of dyes, efficient redox mediators, and metal complexes as well as optimising semiconductor photoanode thin film for the improvement of the sensitiser' performance [5].

Natural dyes are organic compound with a hydroxyl group attached to their nucleus and sparingly soluble in water [6-7]. The solubility parameter represents a quantitative degree of affinity between a solute and a solvent, so it is used as an solubility parameter, polar solubility parameters and hydrogen bonding solubility parameter [6]. The colours of the dyes are due to the presence of various pigments which have been proven to be an efficient sensitiser. Anthocyanin is the core component of some natural dye, and it is often found in fruits, flowers and leaves of plants [8]. Anthocyanins are the polar compounds, which usually extracted by the solvents using acidified aqueous mixtures of ethanol, methanol or acetone [9]. Water-soluble anthocyanins pigments have become increasingly important and have received great interests in research. In this regard, anthocyanins, being a natural colourants, received much research attention in optimizing the purification of these pigments [10]. However, anthocyanin pigments are relatively unstable and often undergo degradative reactions during processing and storage.

In order to achieve a viable stability in the extraction procedures, extraction solvents of these natural dyes must be carefully selected [11]. In this work, we assessed the effects of different dye extracting solvent (acetone, ethanol, mixture of acetone and ethanol (v/v 1:2), and distilled water (DI water)) to extract natural tropical dye of Mulberry, Roselle and Oxalis Triangularis. Mulberry, Roselle and Oxalis Triangularis.

EXPERIMENTAL METHODS

Oxalis Triangularis, Roselle and Mulberry were extracted using grinding based method. Different solvents and optimum conditions were investigated in order to obtain the effectiveness of dye extraction.

Selection of Plant Sources

In order to keep the freshness of the biological materials used to a maximum, each of the material need to be readily available, local origin and easy to manage in a tropical environment, in this context Perlis, Malaysia. The number of possible plant sources is reduced by rigorous selection considering the main aspects as shown in Table 1. The requirements of the dye selection are important thing to be noted as the sources must be able to harvest all over the year. Hence, plant sources, which are Oxalis Triangularis, Roselle and Mulberry (Fig. 1) were selected and locally available in Perlis. All of the three natural sources are belongs to the anthocyanin compound of the pigmentation. The extraction of the natural dye had to be performed by a simple grinding based extraction method.

TABLE 1. The main requirements for a basic set of natural dyes.

Agricultural demands
Reasonable requirements for production and harvesting of the plant material Easy handling and storage of the raw materials High dye sensitiser content Easy extraction with water
Requirements of dye selection
Production of plant material in sufficient amounts with simple agricultural methods including environmental clean extraction methods to obtain dye sensitizer. Formation of a suitable class of dyes which is, in its applicability, comparable to the classes of natural dyes in use at present.

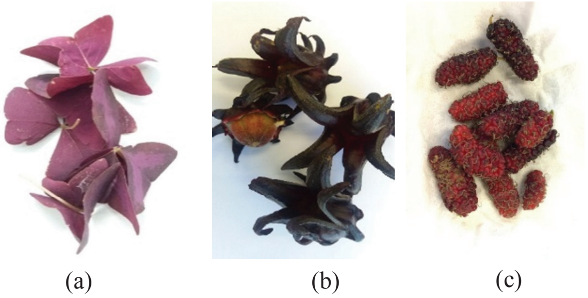

(a) (b) (c)

FIGURE 1. Origin of natural dyes source used in this study, (a) Oxalis Triangularis, (b) Roselle, and (c) Mulberry.

Grinding Based Extraction Method

The organic extraction method was used to extract plant dyes. The cleaned and grinded plants (Oxalis Triangularis, Roselle and Mulberry) are respectively dipped for 24 hours into the extracting solvents which were acetone, ethanol, mixture of acetone and ethanol (v/v 1:2) and DI water, separately. The extracted dyes were stored under darkness conditions to avoid light decomposition [12]. After 24 hours, the dye was filtered from the solid impurities and the extracting solvent were used for characterisation and measurements. In order to investigate the stability of the dye extract, the dyes were stored again at temperature 4℃ for seven days after the first measurement and the dye extract was re-measured again on day seven.

Characterisation of Anthocyanin Compound

Ultraviolet-Visible (UV-Vis) absorption spectra is used to analyse the type of pigments and can be used as an inference of the pigment concentration through the position of absorption peak and intensity, respectively [12]. UV-Vis spectra of Oxalis Triangularis, Roselle and Mulberry were recorded at wavelength 200 to 800 nm. The spectra were taken with a reference of solvents of the dye extraction. However, in order to investigate the stability of the extracted dyes, the extracted dyes were re-measured after seven days they had been stored. The percentage of degradation was calculated using Eq. 1:

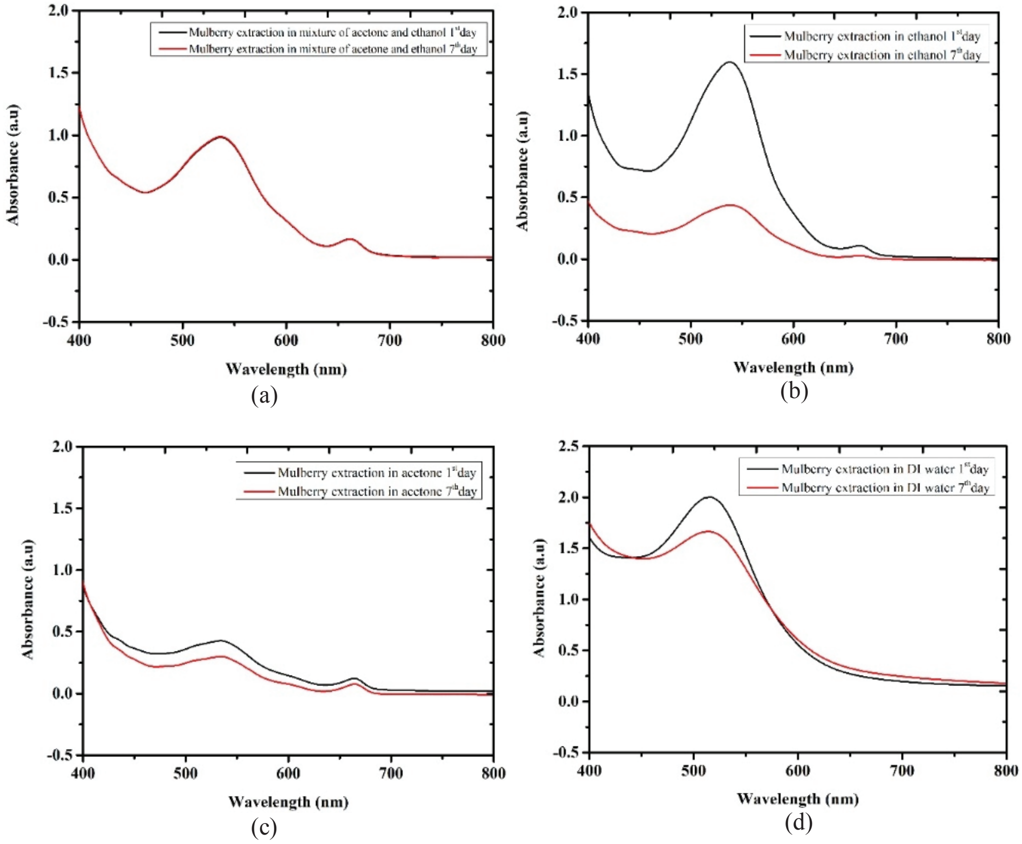
$$\text{\% of degradation} = \frac{A^0 - A}{A^0} \times 100 \tag{1}$$

where, A^0 is the initial absorbance of the sample solution at day 1 of dye extraction and A is the absorbance at day 7 after storage.

RESULTS AND DISCUSSION

Absorption Spectrum in Different Natural Dye Solution

The absorbance spectra of Mulberry, Roselle and Oxalis Triangularis extraction for protic polar solvents like water, ethanol and acetone shows a peak in the range of 500 nm to 700 nm, which indicates the presence of red to blue anthocyanin compound [14-16]. These peaks are observed in the UV-Vis absorption spectra for dye solution extracted using various solvents for Mulberry, which is red in colour as shown in Fig. 2. Figure 2(a) shows the absorption spectrum of Mulberry in a mixture of acetone and ethanol are almost the same even after seven days of storage. The Mulberry in the mixture of acetone and ethanol showed absorption peak at 550 nm which is almost the same result that reported in the previous report [12]. Figure 2(b) shows the most decreasing performance at the 550 nm peak and 670 nm peak of the dye extraction in ethanol after seven days. Figure 2(c) and (d) also show the decreasing performance at the peak of 530 nm, 660 nm, respectively. Mulberry extraction in ethanol shows the highest degradation percentage about 47% while 0% degradation for Mulberry dye in the mixture of acetone and ethanol.



(a) (b)

(c) (d)

FIGURE 2. UV-Vis absorption spectra of dye solutions extracted from Mulberry in different solvents which are (a) mixture of acetone and ethanol, (b) ethanol, (c) acetone and (d) DI water.

Figure 3 shows the absorption spectrum of Roselle extracted in different solvents after seven days of storage. Figure 3(a) and (c) show the decreasing performance at the 540 nm peak and 670 nm peak of the dye extraction in ethanol after seven days. Figure 3(b) shows the highest anthocyanin peak intensity in the range of 500 nm to 600 nm in comparison to other type of extracted solvents. Thus, it shows that the Roselle dye extraction in ethanol has promising stability. However, Roselle dye extraction in DI water shows the most stable anthocyanin compound due to 0% degradation after seven days of storage as compare to in mixture of acetone-ethanol, ethanol and acetone which demonstrate 20%, 67%, 20% degradation, respectively.

Figure 4 shows the absorption spectrum of Oxalis Triangularis extracted in different solvents after seven days of storage. Figure 4(a), (b) and (c) show the high absorbance peak at the range of 400 to 500 nm. Apart from that, the absorption intensity and the absorbance peak of Oxalis Triangularis extracted shows the same pattern in mixture of acetone and ethanol, ethanol and acetone solvents. The stability of the dye extracts depicted that Oxalis Triangularis in mixture of acetone and ethanol and acetone solvent have 50% degradation compared to other solvents. Figure 4(d) shows a broad peak from 500 to 600 nm and low absorbance intensity of Oxalis Triangularis in DI water.

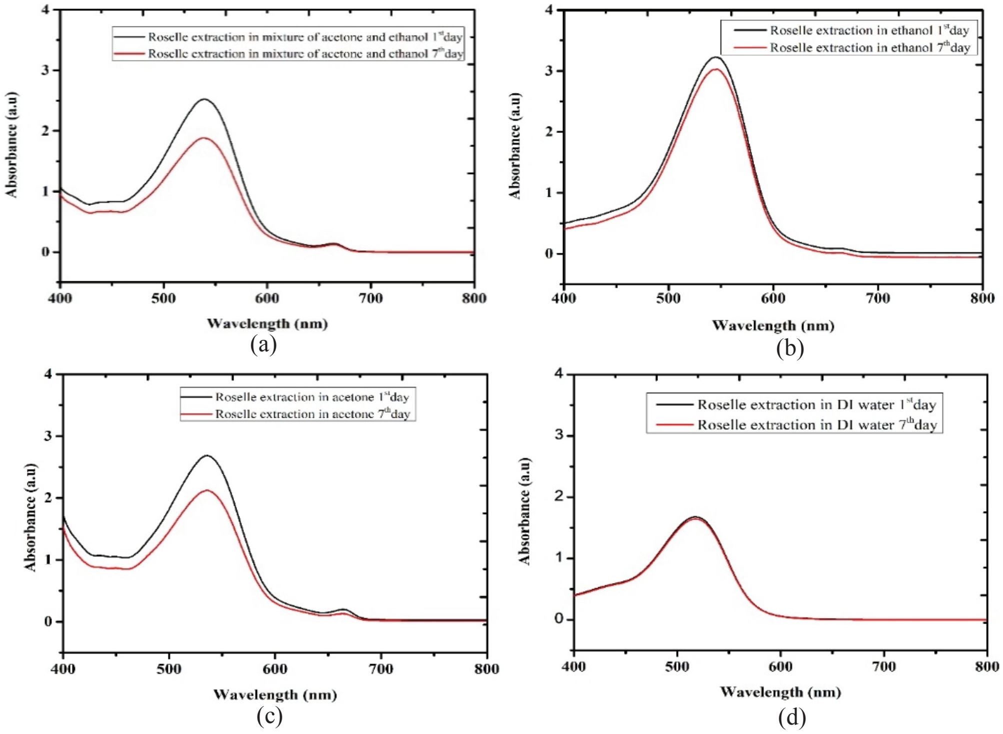


FIGURE 3. UV-Vis absorption spectra of dye solutions extracted from Roselle in different solvents which are (a) mixture of acetone and ethanol, (b) ethanol, (c) acetone and (d) DI water.

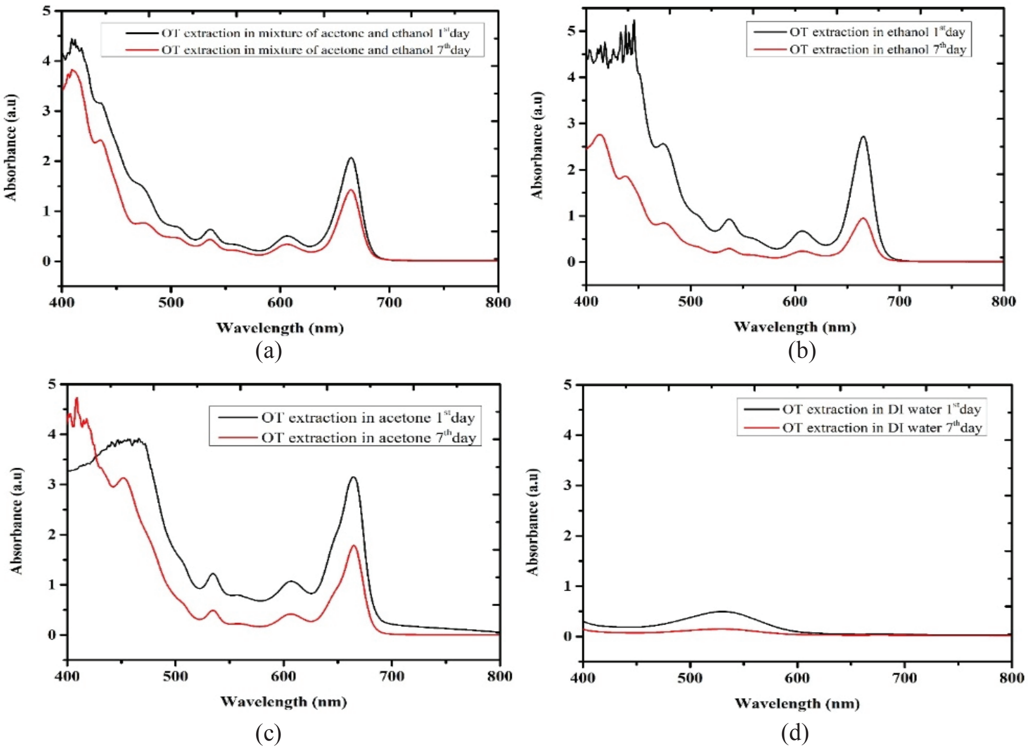


FIGURE 4. UV-Vis absorption spectra of dye solutions extracted from Oxalis Triangularis in different solvents which are (a) mixture of acetone and ethanol, (b) ethanol (c) acetone and (d) DI water.

CONCLUSION

This work revealed that the degradation of the Mulberry, Roselle and Oxalis Triangularis extraction dyes are varies in acetone, ethanol, a mixture of acetone and ethanol (v/v: 1:2) and DI water, respectively. The variation peaks of absorption spectra values may imply the electrostatic interaction between the polar solvent and polar solutes. In this study, it shows that anthocyanin degradation is affected by the solvent used during extraction process. Hence, the results emphasize that anthocyanin compound are relatively unstable and often undergoes degradation during fabrication process and storage. Generally, the anthocyanins and their derivatives show a broad absorption band in the range of visible light attributed to charge transfer transition. In the application of dye-sensitised solar cells (DSSCs), the generation of current-voltage of the fabricated cell depends on the amount of dye adsorbed on the TiO_2 surface, the dye structure, light-harvesting efficiency and electron injection ability of the dye. Therefore, the solvent has to be chosen very carefully for the extraction of dye to produce excellent DSSC performance.

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