Flowers Pigment Extraction from *Erythrina Spp.* and *Ixora Coccinea* Used as Natural Dye in Dye-Sensitized Solar Cells Application

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***Abstract*— Natural dye sensitizer for DSSC extracted from different natural products is been used by researchers to replace synthetic dye however limitations of low efficiencies, poor dye regeneration, and low stability. There are several methods or new natural products from fruits, flowers, seeds, and leaves were approached to help improve the natural dye performance for DSSC. Flowers of Erythrina spp. and Ixora coccinea is selected because of red pigmentation existed in both flowers and its high availability in Malaysia. The research is carried out to identify the best method of flowers pigment extraction process by using different solvents, temperature, and pH by measuring its absorption in visible light range. Methanol solvent was found in this study as the best solvent in the extraction process for *Erythrina spp.* and ethanol for *Ixora coccinea*. High absorption was shown in this study at optimum temperature for *Ixora coccinea* is 80 ˚C and temperature 60 ˚C for *Erythrina spp.* flower. The suitable pH condition for flowers pigment extraction has also been studied where at pH 3.0, *Erythrina spp*. has managed to reach the optimum result, while the natural pH condition at 4.8 is the most suitable for *Ixora coccinea*. Functional groups structures of each flowers sample have been identified, using FTIR, where the hydroxyl, carboxyl, and alkane are found in each sample which show that these natural dyes consist of functional groups of anthocyanin molecule which could help to form bonds with TiO_2 as photoanode of DSSC. This study show that these natural dyes can be utilized as photosensitizers in DSSC due to its wide absorption spectra and its chemical components existed within the pigments.**

Keywords*— DSSC Sensitizer, natural dye, solvents, temperature, pH

I. INTRODUCTION

DSSC is a promising device in the third generation of photovoltaic technology developments due to its ability to absorb photons from sunlight and convert it into electrical energy in diffused light source with an easy preparation method, environmentally friendly and high availability [1]. Due to highly beneficial effects and infinite energy resource, DSSC becoming one of option as the main energy resource in the future to replace fossil fuels, which progressively reduced. DSSC standard structure consists of a semiconductor nanocrystal electrode-absorbing dye as photoanode, counter electrode and electrolyte containing iodide and tri-iodide ion. Each component played important role, but this study will be focusing on the dye sensitizer. The dye sensitizer role in DSSC is to absorb photon from sunlight and produces photo-excited

electrons then transfer it to conduction band of TiO_2 [2]. In 1988, Michael Grätzel and Brian O'Regan managed to create a DSSC device with efficiency of 12% in diffuse light condition also known as Gratzel cells, using ruthenium dye as sensitizer [3]. Since the discover its capability to works in diffused light, numerous advances were studied specifically different types of sensitizer were synthesized and studied such as metal complex sensitizers, metal-free organic sensitizers, and natural sensitizers[4].

Natural sensitizers were obtained from trees, fruits, flowers and seeds. There are numerous types of natural products that had been studied and synthesis by other researchers to be used as DSSC sensitizer when S. Hao et al and Thambidurai et al. also studied *Erythrina spp*. and *Ixora coccinea* as dye sensitizer for DSSC and obtained efficiency of 0.55% and 0.33% respectively[5][6]. Those studies shown both flowers have capabilities to be used as DSSC sensitizer, but the low efficiencies compare to artificial sensitizer show that there are several limitations of amount of color pigments was extracted from the flowers due to the nature of impurities of natural products[7].

The flowers petals as seen in Fig. 1 are in color of red pigment which shown anthocyanin and carotenoids existed in their chemical compounds where it probably will help the sensitizer attached onto TiO_2. M. Al. Alwani et al was used *Alternanthera dentata* leaves and *Musa acuminata* bracts extracts as DSSC sensitizer then obtained efficiencies of 0.15% and 0.31% respectively by carried out study of effect of solvents, temperature and pH on dye extractions[8]. The optimum experimental condition was chosen by the highest absorption curve spectra. Therefore, in this research flowers of *Erythrina spp.* and *Ixora coccinea* will be undergo the study of the effect of solvent, temperature, and pH to improve the dye extraction performances.

Anthocyanin and carotenoids are helps to reflect red light which is anthocyanin reflect light wavelength spectra of 400 nm to 600 nm while carotenoids reflect at 400 nm to 550 nm. Most plants and flowers consist of chlorophyll which is helps in photosynthesis process. Chlorophyll consists of two different types namely as chlorophyll a and chlorophyll b. Chlorophyll a absorbed blue-violet and orange-red light lies at 675 nm while green light is reflected by chlorophyll b by absorbing light at wavelength of 640 nm which mostly giving the plant's leaves in green color[9]. All the pigments spectra behavior was assured by the fig. 2 [10].

(a) (b)

Fig. 1. (a) *Erythrina spp.* and (b) *Ixora coccinea* flowers

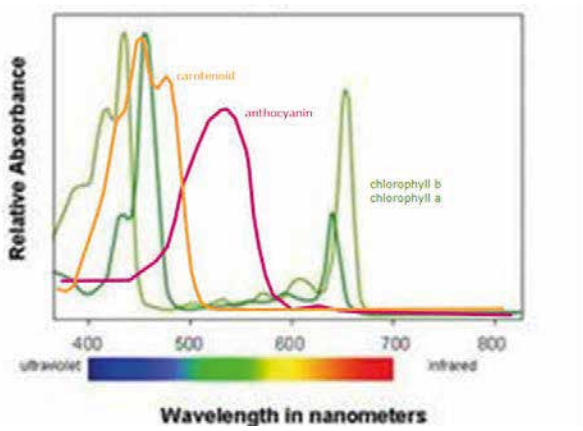

Fig. 2. Photosynthesis absorption [10]

In this paper, the optimum conditions of natural dye extractions were obtained when both flowers were extracted under variations of solvents, temperatures and pH level by observing absorption spectra. These approaches are to improve the amount color pigment extracted from the natural dye before to be used as DSSC sensitizer.

II. Experimental

Erythrina spp. and *Ixora coccinea* flowers sample is washed with distilled water to remove any unwanted impurities and then dried in the oven for 30-60 minutes at 50 ˚C to remove any additional water which can interfere extractions process. Dry samples were cut into smaller pieces and pounded using a mortar to turns the sample into powder form which helps to increase the area of extractions. Each flower in powder forms are separated by weighing separately at 10 g research conditions of solvents and 5 g for different temperature and pH study respectively.

Four different types of solvents of ethanol, methanol, acetonitrile and chloroform with ratio of 1:10 of sample weight to solvent volume was used to study the effect of solvents in dye extractions. The sample is left for one day in a dark place at room temperature. After 24 hours, the sample was filtered using filter paper (NICE, 12.5 cm, 102 Qualitative) to separate the residue flowers from solvents extract which then the extract can be used to absorption measurement. The outcome obtained from solvents study which solvent with high absorption and wider spectra was used for next research of temperature and pH. All absorption analysis for solvents, temperature and pH was carried out using PerkinElmer UV-Vis spectrometer Lambda 35 was used to study the absorption strength at certain wavelength range of 400 nm to 750 nm. Then, the solvent for each flower, then filtered and purified by heating in an oven at 50 °C until the sample evaporates and dries into flakes. The flakes will then be used in the analysis by FTIR spectrophotometer. FTIR spectra was measured with Perkin Elmer Spectrum 400 FT-IR/FT-NIR & Spotlight 400 imaging systems on wavenumber 4000 cm^{-1} to 650 cm^{-1}.

The study was continuing with the effect of temperature study where the 5 g of each flower's powder were put into an Erlenmeyer flask with the optimum solvent obtained from early study of different solvents with 1:10 ratio. Then, a magnetic stirrer is put inside flask and heated on a hot plate with an angular velocity of 350 rpm at temperature 40, 60 and 80 within one hour. After one hour, the sample extract is filtered then can be used for absorption measurements.
Extraction process for different pH conditions are carried out using the separated 5 g sample of flowers by soaked it into the optimum solvent obtained from solvent study. Sodium hydroxide and hydrochloric acid are used to control a predetermined pH of 3 and 8. After that, the samples stored and kept in a dark place for one day. The sample was then filtered using filter paper to remove the residual flowers and placed into test tube for UV-Vis spectrophotometer analysis.

III. Result and Discussion

A. UV-Vis Absorption Spectrum Using Different Solvent

The UV-Vis absorption spectrum for the sample in different solvent for *Erythrina spp*. and *Ixora coccinea* shown in Fig. 3 where both reacted in blue shift behavior where high absorption occurred in short wavelength and decreasing towards increasing wavelength in visible light range from 400 nm to 700 nm. From Fig. 3, *Erythrina spp.* and *Ixora coccinea* shown have high absorbance when extracted using methanol and ethanol respectively. A small intense peak for *Erythrina spp.* seen at 665 nm while the absorption spectra decreasing with increasing wavelength. This indicates a small amount of chlorophyll can be found inside the flower petals which helps in photosynthesis processes[11]. A broad peak wavelength spectrum seen for *Erythrina spp* in ethanol and methanol solvent within 500 nm towards 640 nm which indicators of the existent of anthocyanin and carotenoids which helps to reflects red colors from the flowers petals. The spectra behavior is seen in Fig. 3 (a) shown both ethanol and methanol help to extracts most of anthocyanins which can be used as the carbonyl and carboxyl group attached onto TiO_2 surface compare to dye extract from acetonitrile and chloroform. *Ixora coccinea* flower have different spectra compare to *Erythrina spp*. where shown in Fig. 3 (b) occurs from 400 nm towards 650 nm in blue-shift behavior. A broad-spectrum peak from 410 nm to 510 nm and small constant absorbance peak seen from 510 nm to 550 nm probably signify anthocyanin and carotenoid present in the dye extracts in ethanol, methanol and acetonitrile solvent. The absorption character of carotenoids highest peaks can be seen at 455 nm for ethanol, methanol and acetonitrile extract.

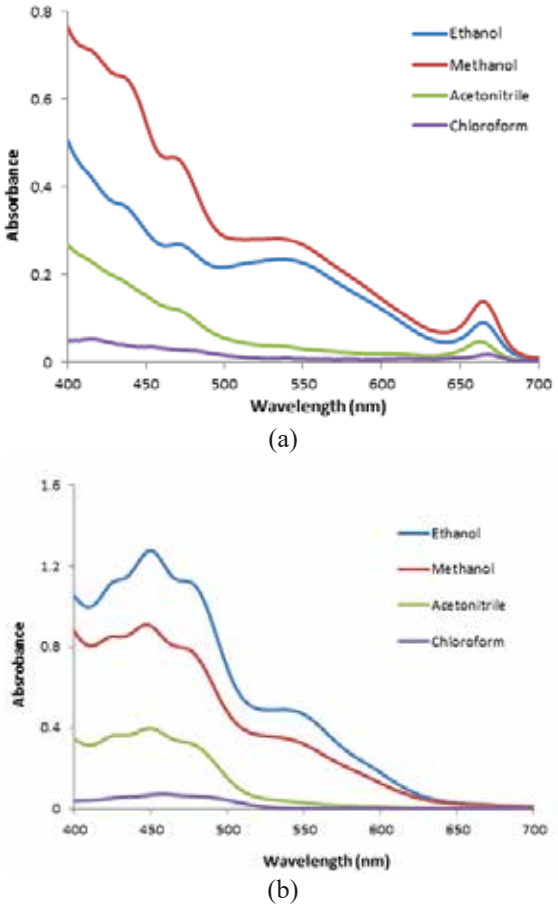

Fig. 3. UV-Vis absorption spectrum of (a) *Erythrina spp*. and (b) *Ixora coccinea* using different solvent

B. UV-Vis Absorption Spectrum Using Different Temperature

The study of temperature effect on dye extraction was completed at temperature of 40˚C, 60˚C and 80˚C and observed in visible light range. The absorption spectra obtained for both flowers spectra shown in Fig. 4 which the highest spectra performance for *Erythrina spp*. and *Ixora coccinea* occurred at temperature of 60˚C and 80˚C respectively. *Erythrina spp*. absorption spectra at temperature of 60˚C have a perpetual absorbance peak from 483 nm towards 530 nm which indicates the existence of anthocyanin and carotenoid in the dye extract. If compare with the study of solvents in Fig. 3(a), after the extract undergo in each temperature, the small intense peak at 665 nm indicates of chlorophyll was not seen in Fig. 4(a). This shown when the dye extracts undergo different condition of extraction, different pigments were extracted. *Ixora coccinea* has a wide spectra peak at 525 nm which imply anthocyanin present in the dye.

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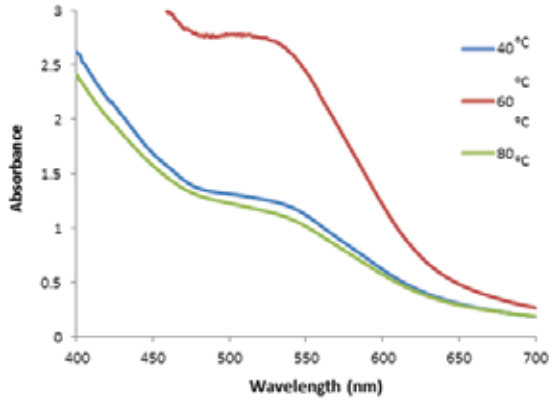
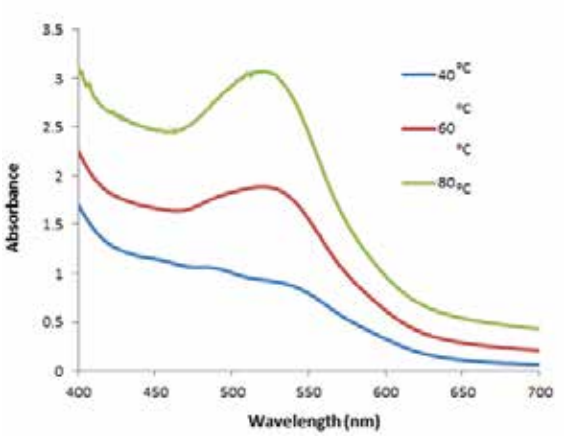
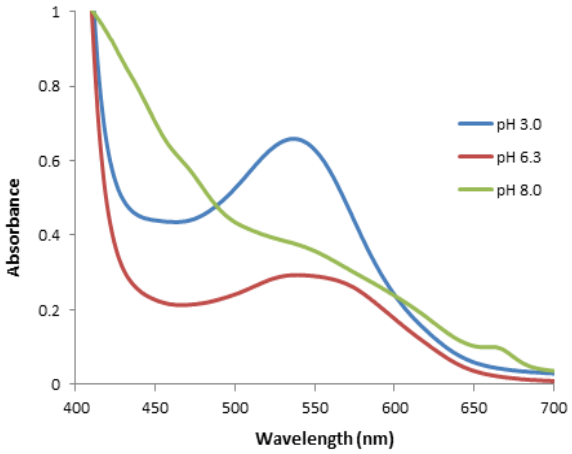


(a)

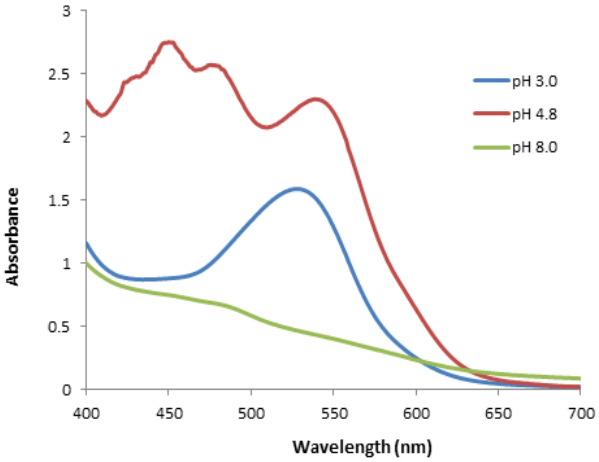


(b)

Fig. 4. UV-Vis absorption spectrum of (a) *Erythrina spp*. and (b) *Ixora coccinea* at different temperature



(a)



(b)

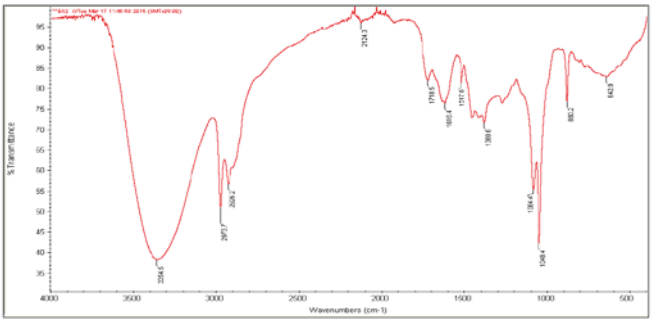
Fig. 5. UV-Vis absorption spectrum of (a) *Erythrina spp.* and (b) *Ixora coccinea* at different pH value

C. UV-Vis Absorption Spectrum in Different pH values

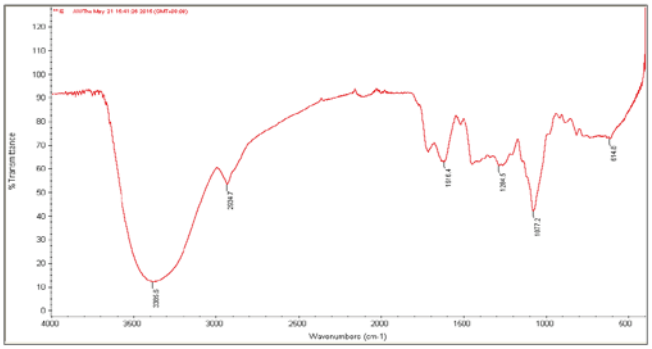
Another study was undergoing in different pH values at 3.0, 8.0 and without adding any acid or alkali inside the extracts. *Erythrina spp.* and *Ixora coccinea* extracts have a natural conditions pH values at 6.3 and 4.8 respectively which is in a mild acidic condition because below than natural values of 7. The highest spectra performance for *Erythrina spp.* and *Ixora coccinea* was at pH values of 3.0 and 4.8 respectively. The absorption spectra for *Erythrina spp.* at pH value of 3.0 shown in Fig. 5 (a) has a peak at 540 nm which represent of anthocyanin pigment. *Erythrina spp.* at pH value 6.3 have the same behavior of spectra at pH value of 3.0 but with lower peaks. The more acidic condition helps to improve more additional anthocyanin extraction. However, *Erythrina spp.* at pH value of 8.0 does not have the same peak locations which assumed the addition basic condition reduce the pigments extractions. Multiple peaks were seen at the absorption spectra for *Ixora coccinea* at pH value of 4.8 which is occurs at 425 nm, 452 nm, 480 nm and 544 nm. All those peaks are occurred within the range of anthocyanin and carotenoid reacted towards lights. When pH values of *Ixora coccinea* was changes into 3.0 and 8.0, the absorption spectra performance was degraded compare to pH value of 4.8. These occurred due to additional acid and alkali solution destroy certain pigments therefore low absorbance performances. This study show that the sensitizer has higher absorption in acidic medium compare to base medium [12].

D. Chemical compounds inside natural dye extracts

When *Erythrina spp.* and *Ixora coccinea* undergo different solvents, temperature and pH value, all the previous spectra graph indicates anthocyanin, carotenoids and chlorophyll by numerous peaks at certain wavelengths. All the pigments can be helping the sensitizer anchoring onto TiO_2 using carboxyl and hydroxyl groups existed at their chemical compounds



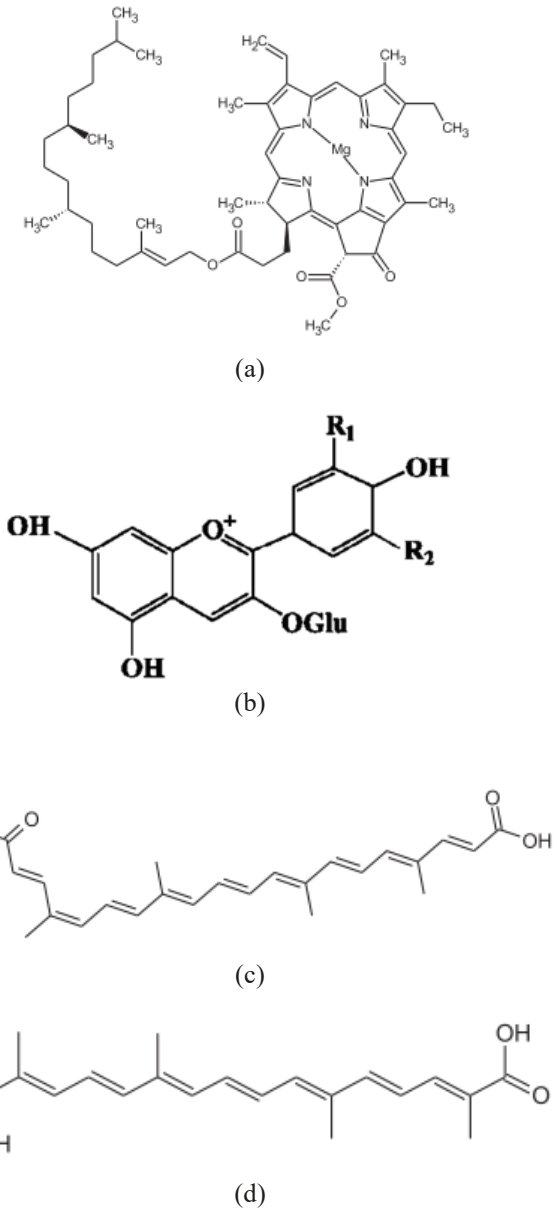
(a)



(b)

Fig. 6. FTIR spectrum of (a) *Erythrina spp.* flower and (b) *Ixora coccinea* flower

[13]. The chemical compounds can be study from FTIR measurement which its represented by wavenumbers. Fig. 6 (a). shows the analysis result of FTIR spectrum on *Erythrina spp.* flower extract. A strong and broad band at 3355 cm^{-1} shows that the existent of O-H with a H-bonded. A functional group of alkanes was indicated by small distinct stretch peaks at 2974 cm^{-1} and 2926 cm^{-1} represent C-H and a bending peak at 1381 cm^{-1} show -C-H. The alkyne functional group with -C≡C- bond can be found at stretch peak at 2124 cm^{-1}. Carbonyl functional group of C=O bond is represented at the strong peak of 1719 cm^{-1}. Other functional group with C=C-C bond with aromatic ring at 1616 cm^{-1} is known as Alkenes and C-O bond at 1084 cm^{-1} and 1048 cm^{-1} which has ether functional group. FTIR test result for *Ixora coccinea* flower is shown by Fig. 6(b). Some of the important wavelengths from result are recorded. Type of the functional group found in the flower extract are alcohol group at of 3386 cm^{-1} wavelengths with O-H bond then functional group of alkanes with C-H bond at 2935 cm^{-1}. C=C bond provided by alkene with 1616 cm^{-1} and Ester functional group which has C-O bond is also shown at 1285 cm^{-1} and 1077 cm^{-1}. The FTIR results for both flowers show that each extract consists several functional groups that could help the dye extract applied as DSSC sensitizer. All the functional groups especially carboxyl and hydroxyl are essential for a sensitizer anchored onto TiO_2 surface. All the chemical compound was presented at FTIR spectra graph are contributed by chlorophyll, anthocyanin and carotenoids seen as Fig. 7.



(a)

(b)

(c)

(d)

Fig. 7. Chemical structure of (a) chlorophyll a (b) anthocyanin and carotenoids consists of (c) bixin and (d) crocetin

IV. Conclusion

The flowers pigment extraction process of *Erythrina spp*. and *Ixora coccinea* as photo dyes used in the application of photocells or DSSC has been successfully carried out. This study show that the dye extraction can be the affected by the solvents, temperatures and pH levels. The effect of the conditions is changes of absorption spectra therefore influence the different amount of pigments such as anthocyanin, carotenoids, and chlorophyll were extracted. The chemical compounds or hydroxyl and carboxyl was proven in FTIR spectra.

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