Fatima H. Malk ✉; Mohammed T. Obeed; Tahseen Alaridhee

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Optical Characteristics of natural Pigment of Portulaca Grandiflora

Fatima H. Malk[a], Mohammed T. Obeed[b], and Tahseen Alaridhee[c]

Department of Material Science, Polymer Research Centre, University of Basrah, Basrah, Iraq

[a] Corresponding author: fatima.malk@uobasrah.edu.iq
[b] Mohammed Obeed@uobarah.edu.iq
[c] tahseen.alaridhee@uobasrah.edu.iq

Abstract. In this work, we investigated the optical properties of natural dye extracted from the portulaca grandiflora flower. The eco-friendly solvent was used through the extraction dye process. The FTIR analysis was conducted to get functional group profile for the natural dye. The Ultraviolet-Visible spectroscopy was performed on the dye thin-film including the absorption spectra, absorption coefficient, refractive index, extinction coefficient, as well as the optical bandgap. The UV-Vis range showed a broad absorption band, including significant bandgaps. The pigment under investigation has narrow indirect bandgap of 1.54 eV and an Urbach energy of 5.33 meV.

INTRODUCTION

Since antiquity, dyes have been a vital role everywhere throughout the globe. Natural dyes are colors obtained from nature that have not been chemically processed. Natural dyes can be derived from a variety of sources, including plants, minerals, insects, and/or animals. Natural dyes are becoming increasingly relevant because they have minimized the environmental pollution, simply extracted, generally available, produced in a green manner and ecologically beneficial [1-5]. These properties enable their use in a variety of applications, including pH [6] indicators, dye-sensitized solar cells [7], and optoelectronic systems [8]. The goal of researchers in this field was to make natural dyes behave like semiconductor materials to improve the efficiency of photoconduction limit. Researchers are presently working to improve dye extraction from plant components such as seed, petals, bark, and leaves, to a marked increase in the rate of productivity [9-11]. Natural dyes have a significant role in photosensitizers, due to their strong light gain and absorption efficiency. The fascinating optoelectronic features of the dye result from the reaction of its electronic structure with light and the difference in the energies. As a result, the highest absorption in the spectrum is caused by transmitted or reflected light [12,13]. The efforts were developed to utilize natural dyes/pigments as semiconductors by enhancing the electron transfer ability in the valence- conduction bands. A number of researchers have reported that natural dyes have been found to be easily derived from several natural plants [14-23]. Flowers are one of the most important sources that contain important elements to form the coloring. The latter is due to the organic compounds containing anthocyanins, chlorophyll, cyanidins, tannins, carotene, luteol, violaxanthol and phycoerythrins [24-28]

Anthocyanin is the primary pigment of the majority cyanic colors, including the violets, reds, scarlets, and dark blues found in the flowers, petal, or plant leaves. [29]. The major objective of this study was to investigate the optical properties of dye thin film. We start with the extraction process using a distilled water as a solvent. The dye extracted in this study has been analyzed and carried out using FTIR and UV-Vis spectroscopy. The findings provided in this paper would help to promote the development of techniques that employ green materials into optoelectronic systems.
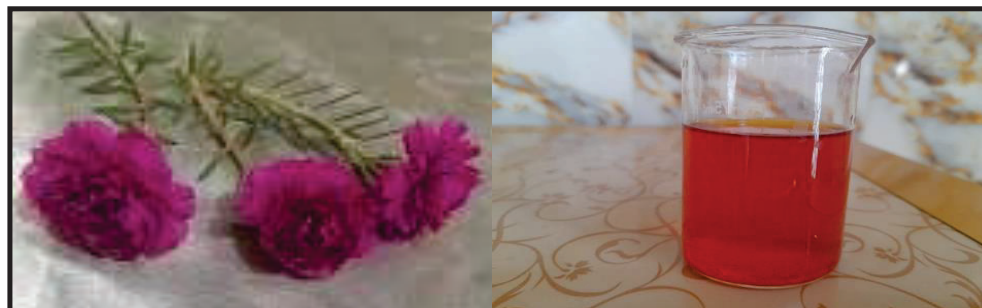
<center>(a)   (b)</center>

FIGURE 1 The portulaca grandiflora flower and visual appearance of its extracted dye.

MATERIALS AND METHODS

Portulaca grandiflora has been used in crude dye extract. This plant is widely located in home and public gardens of Basrah city. A magnetic stirring (BOECO Hot Plate Magnetic Stirrer, model MSH 420) was used in pigment extraction process. The stirring max volume of the magnetic stirrer is up to 15 L, with the stirring speed of 60-1110 rpm and a heating ambient temperature to 450 ℃.

The Shimadzu IR Prestige 21 ranging from 200 to 4000 cm^{-1} was used to obtain the FTIR spectra. The GBC Cintra 2020 UV-Visible spectrometer was used to record the ultraviolet visible spectra in the wavelength range of (200-1100) nm.

Dye Extraction Procedure

Before beginning the extraction, several flowers were collected, about of 250 g. The petals of the flowers were cleaned with distilled water to wipe down and eliminate any dust particles. After that, the cleansed layers were stored for 10 days at room temperature in a dark and dry environment before being pulverized in a crusher to get a powder form. The powdered product (2 g) was immersed in 50 ml of distilled water in a covered glass beaker and filtered with Paper with medium-fast filters weighting 55 g/m^2 and 0.33 mm to obtain an aqueous extract of portulaca grandiflora flower. The natural dye and water solvent were mixed in a 1:50 ratio. The magnetic stirring process parameters were adjusted at 50 ℃ for 60 minutes. Figure (1a) depicts the liquid colors extracted from portulaca grandiflora flower.

Preparation Process of Thin-Film

The glass slide of dimension 2.5 × 7.5 cm was cleaned with distilled water and acetone to be ready for casting process of the resulting solution. The sample was dried in an electric oven set to 50 ℃ for 20 minutes. For casting, spin coating method was used for multiple rotations (1000 rpm/min) throughout the coating process. The final coated samples were homogeneous in thickness (200 nm) and pure enough to ensure their acceptability (see Fig.2).
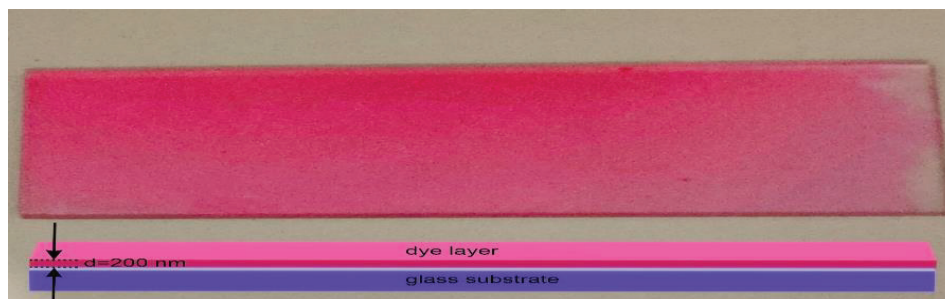
FIGURE 2: The portulaca grandiflora dye in coated-substrate and schematic diagram of the extracted dye thin film and its thickness.

Analysis of The FTIR Spectroscopy

The structure of natural dyes was characterized by FTIR analysis, as illustrated in Figure 3. A different bond of the FTIR spectra, has been listed in Table 1. The active group are observed in two ranges of 3100 – 2000 cm^{-1} and 1600 – 400 cm^{-1}. In Figure 3, distinct absorption bands represent the interaction between electromagnetic wave and substance in the molecule. The single bond observed at 3071 cm^{-1} is the CH stretch sp^2. The natural
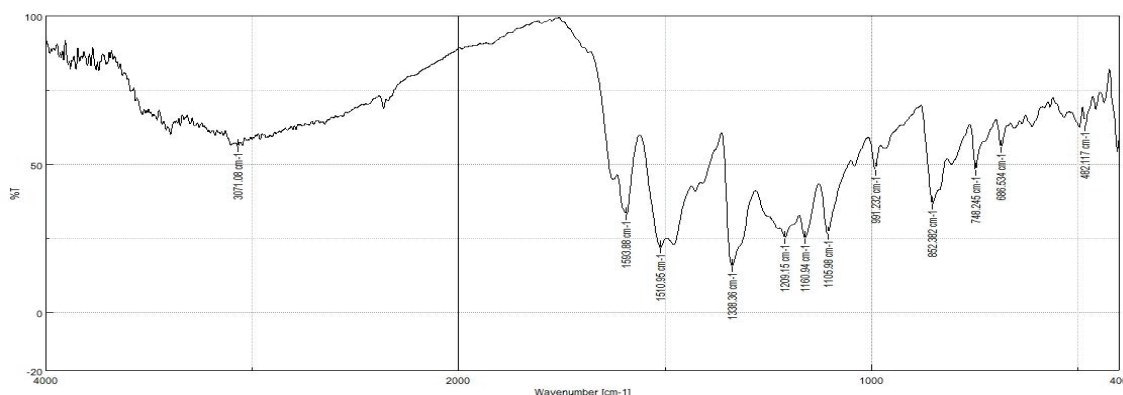

FIGURE 3: The FT-IR spectroscopy of as extracted natural dyes at room temperature

component of flower dye, which contains flavonoids, fatty acids, saponins, and tannins, led to the C–H absorption maxima. The absorption bands located at 1593 and 1510 cm^{-1} are attributed to the aromatic C=C stretch vibration. The strong intensity peaks at 1209, 1160 and 1105 cm^{-1} correspond to the presence of C–O alkoxy stretch. Additionally, A band with isotropic properties detected at 1338 cm^{-1} is for –CH_3 bending group. Furthermore, the absorption peak at 991cm^{-1} is due to the bending stretch of the C–O group. The findings obtained match well with the previous work [30-33].

RESULT AND DISCUSSIONS

UV-Vis spectroscopy. The UV visible spectra (absorption and transmission) of the dye sample were measured in wavelength range between 300-900 nm and shown in Figure 4. The thin films of dye were exposed to UV-visible spectrophotometer (CE-7200) double beam
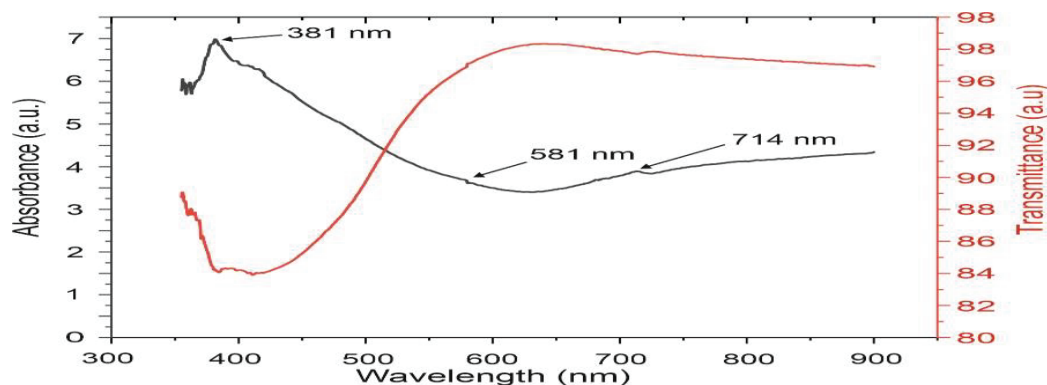

FIGURE 4: Optical absorption (black curve) and transmittance (red curve) spectra of extracted dye as a function of wavelength (nm).

spectrophotometer at room temperature. From the spectra presented in Figure 4, it was observed that the portulaca grandiflora dye has a weak absorption that occurs around 381 nm and continues almost steady till the end of the visible region. The behavior of the absorption spectra in the visible region is due to the anthocyanin dye resource which allows to be utilized as a photosensitizer for DSSC. The thin film under study can transmit large portion of visible light as shown in Figure 4. The absorption peaks in the 400-500 nm range of wavelength often

refer to the excitation of $n \rightarrow \pi^*$ because of the low energy requirements. This kind of transition is known as the R-band, is formed in a molecule by unsaturated chemical groups (chromophore groups).

Optical Absorption coefficient and Optical Energy Gap.

The absorption coefficient is particularly significant in the absorption region to identify the type of electronic transfer that occurs in the electronic structure of the substance [34]. The absorption coefficient was calculated using the equation below.

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right] \tag{1}$$

The indices R and T are the reflection and transmittance, respectively. and the film thickness is expressed by d. The latter parameter is obtained using the conventional approach, that includes the values of the mass of both the glass substrate m_1, and the dye layer on that substrate m_2 as described below:

$$d = \frac{m_2 - m_1}{\rho\, a} \tag{2}$$

The density of the dye and the area of the sample are represented by ρ and a, respectively. Figure 5(a) depicts the absorption coefficient of dye under study. The spectra show one major absorption band at about 350-435 nm that results from $n \rightarrow \pi^*$ electronic transitions of dye components. The absorption coefficient generally leads to the identification of the energy band gap. The Homo-Lomo energy E_g is one of the most essential physical factors in semiconductors and dielectric properties. The optical gap refers to the production of a distinct, hole

and uncorrelated free electron with the minimal quantity of energy. The energy gap effect is related to the mobility of individual particles in solids. In this investigation, the energy gap values are calculated using the intercept of $(\alpha h\upsilon)^\gamma$ versus $h\upsilon$ with the x-axis. The latter treatment is described by applying the Tauc's relationship which is defined in Eq. 3 below [35]:

$$\alpha = \frac{A\{(h\upsilon - E_g)\}^\gamma}{h\upsilon} \tag{3}$$
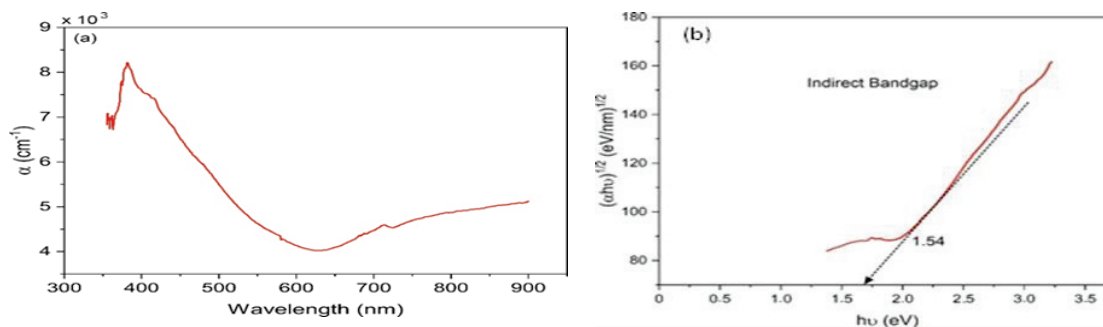
FIGURE 5: (a) Absorption coefficient of thin film where (b) represents indirect bandgap using Tauc relation.

where A represent the transition probability dependent constant, and is the distribution of the density of states index which has different values basing on the transition mode (direct or indirect). The plot of (h)versus hfor portulaca grandiflora sample is presented in Fig. 5(b). The energy value is about 1.54 eV for sample deposited at room temperature. The kind of energy is obtained due to appear new localised atomic energy levels below the conduction band of natural dye. The defect bands give rise to emerge a localised tail states which are preferable to collect electrons at "Urbach region" in both valance and conduction band states. The Urbach energy of a system is connected to its structural disturbance function [36]. The higher the Urbach energy, the more disorders result from insufficient crystalline or amorphous structures. As shown in Figure 7, the estimated Urbach energy of Portulaca grandiflora thin film is 1.94 meV. The observed modifications in material could be due to the internal fields governing the interaction of chemical groups or diminished capacity or a to convert weak bonds into defects.

Refractive Index and Extinction Coefficient.

One of the key characteristics to identify the optical properties of a sample are refractive index and extinction coefficient. For the examination of dyes or substances, the optical factors n and k determines how powerfully the compound attenuates light at a specific wavelength. These indices can be combined into a complex frequency-

dependent equation, in which n and k stand in for the real and imaginary components, respectively. The following relationships Eqs. (4 & 5) has been used to calculate n and k parameters [37].

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2}$$ (4)

$$k = \frac{\alpha\lambda}{4\pi}$$ (5)

Figure 6(a) shows how the refractive index for natural dyes varies as a function of wavelength.

From a comprehensive view of that figure, the refractive index of the organic dye had a value of (1.54). Furthermore, a distinct divergence was seen in the visible region. The considerable value of n at high energy region are caused by the influence on the absorption of light beyond 400 nm [38]. The extinction coefficient k was determined for the pure portulaca grandiflora dye thin-film (see Fig. 6(b)). The extinction coefficient, as is well known, represents the photonic material and its qualities to light. The natural dye displays the increase in the extinction coefficient value with increasing the wavelength due to the diffusing effect.
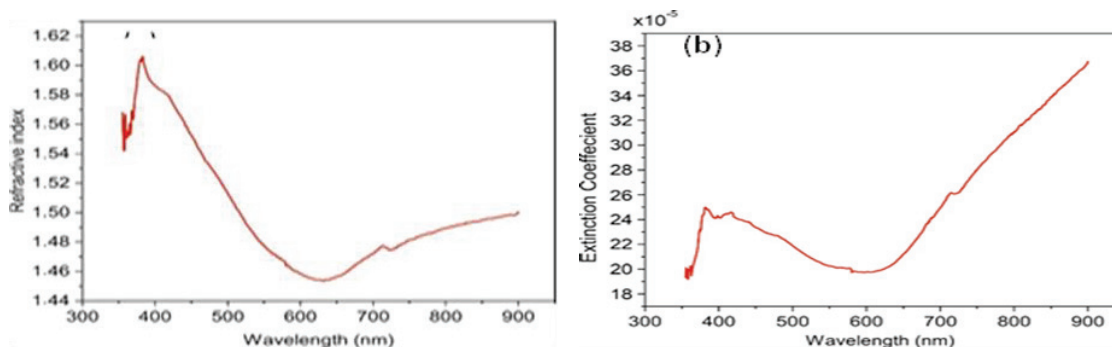

FIGURE 6: Refractive index (a) and the extinction coefficient (b) of natural dye thin film.

CONCLUSIONS

The results of this study have shown that dye from Portulaca grandiflora may be isolated utilizing low-cost techniques as a promising resource. A good yield was seen when applying a water bath and magnetic stirrer extraction. Due to the absorption coefficient calculation, the indirect bandgap was adopted which was 1.54 eV, whereas Urbach energy was 1.94 meV. The FTIR data were used to identify the solvent's influence on natural dye extraction, as well as distinct functional groups. The work conducted in this paper will significantly contribute to new insights into the optical properties of organic dyes towards optimization of optoelectronic properties.

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