

Optical properties of natural dyes: prospect of application in dye sensitized solar cells (DSSCs) and organic light emitting diodes (OLEDs)

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Abstract

Optical properties (absorbance, fluorescence, and transmittance) of the natural dyes extracted from flower, leaf, bark and rhizome of some plant species available in Nepal have been explored, with the prospect of application in dye-sensitized solar cells (DSSCs) and organic light emitting diode (OLED) employing UV-Vis., Fluorescence and FTIR Spectroscopy. The extraction process was carried out using solvents with a varying polarity index of ca. 0 to 10: cyclohexane (CH), dichloromethane (DCM), acetone, ethanol (EtOH), methanol (MeOH) and double distilled water (DDW). The absorbance was found to depend on the nature of solvent used; the dye samples, *A. vasica* Nees (in DDW, acetone, DCM and CH), *N. arbor-tristis* L (in MeOH and CH), *U. dioica* L (in EtOH, acetone, DCM and cyclohexane), *O. wightiana* Wall (in acetone and CH), *A. vulgaris* L (in DCM and cyclohexane), *C. coccinea* Wall (in DCM), *R. anthopogon* D.Don (in DCM) and *W. fruticosa* L (in CH), showed good absorbance in the visible-region and blue shift in the absorbance maxima was noticed with increase of the polarity index of solvents. Some plant extracts showed intense fluorescence emission in the visible region, which hints at their prospect of application in the OLED devices.

1. Introduction

Nepal, with its diverse flora, is a storehouse of economically important plant species which can have high potential applications in drug synthesis, textile dye, and cosmetics. Traditionally many of the plant species such as *Acacia nilotica* Linn., *Alnus glutinosa* Linn., *Althaea rosea* Cav., *Curcuma longa* Linn., *Lawsonia alba* Linn. and *Woodfordia fruticosa* Kurz have been utilized to extract natural dyes (Gokhale *et al.*, 2004) in these regards. Also, as natural dyes are colorants they also have prospects of employing as a light absorber (sensitizer) in DSSC and also as a fluorescence emitter in OLED: In DSSCs, these materials are considered promising for utilizing as a sensitizer instead of less environmentally friendly organo-metallic complexes (e.g., Ruthenium dye). In this connection, some of the dyes used as sensitizer are cyanin, anthocyanin, tannin, chlorophyll, betalains, carotenoids (Gao *et al.*, 2000; Sirimanne *et al.*, 2006; Fernando *et al.*, 2008; Calogero *et al.*, 2010).

The first DSSC, which belong to thin film solar cells,

was realized with a chlorophyll sensitized zinc oxide (ZnO) electrode in 1972 and is considered to be a promising means toward harvesting solar energy in low cost (EIER, 2006). In particular, it comprises a thin film of a compound semiconductor with a wide bandgap (mostly titanium oxide (TiO₂) or zinc oxide (ZnO)) on top of which a dye is coated for photosensitization. This kind of photo-cell is also known as the "Grätzelcell", which was originally co-invented in 1988 by Brian O'Regan and Michael Grätzel (O'Regan and Grätzel, 1991; Nazerruddin *et al.*, 1993; Grätzel, 2003). In DSSCs, when a dye molecule is photo-excited, the electron jumps from HOMO to LUMO level of dye. If the LUMO of dye matches with the conduction band of the compound semiconductor electron hops to the later material, reach to load and eventually recombines with the ionized dye molecules with the aid of electrolyte.

With TiO₂-based dye-sensitized solar cells, a maximum of 14% efficiency has been achieved using standard ruthenium polypyridyl complexes as a sensitizer in the laboratory condition (Nazeeruddin *et al.*, 2005;

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Qin and Peng, 2012). Further improvement in photovoltaic properties and durability of these kinds of cells by utilizing an appropriate sensitizer would certainly facilitate widespread utilization of this technology.

There are several studies that employ the natural dyes as a sensitizer (Hao *et al.*, 2006; Chang and Lo, 2010; Susanti *et al.*, 2014) but the downside is that they have low efficiency. This problem can be circumvented by identifying natural dyes which increase the performance efficiency. For example, Susanti *et al.*, 2014, has reported the performance of photo-cells fabricated with ZnO and tamarillo fruit as a sensitizing dye. Similarly, the extracts from spinach and ipomoea were used as good natural sensitizers for dye sensitized solar cells (Chang *et al.*, 2010). Higher incident photon to current conversion efficiency (IPCE), which is proportional to the absorption coefficient of the dye, over the visible and near IR region of the solar spectrum, is one of the necessary conditions to achieve enhanced solar cells performance. Therefore, this study has focused on identifying the natural dyes which show good absorbance over the visible and near-IR regions.

2. Materials and methods

Extracts of natural dye from fifteen plant species (flower, leaf, bark, and rhizome) were obtained with the solvent extraction method using both the polar and non-polar solvents; double distilled water (DDW), methanol (MeOH), ethanol (EtOH), acetone, dichloromethane (DCM) and cyclohexane (CH). The plant samples collected for extraction of natural dyes were: 1. *A. vasica* Nees (local name: Asuro, leaf), 2. *A. vulgaris* L (Titepati, leaves), 3. *B. aristata* DC (Chutro, bark), 4. *M. esculenta* Buch Ham (Kaphal, bark), 5. *N. grandiflora* DC (Jatamarsi, rhizome), 6. *U. dioica* L (Sisno, leaves), 7. *J. humile* L (Jaai, flower), 8. *R. arborium* L. (Laliguras, bark), 9. *O. wightiana* Wall (Nundhiki, leaves), 10. *N. arbor-tristis* L (Parijat, flower), 11. *C. coccinea* Wall (Sano Tusare, bark), 12. *A. vasica* Nees (Asuro, flower), 13. *R. anthopogon* D.Don (Sunpati, leaves), 14. *B. ceiba* L (simal, flower) and 15. *W. fruticosa* L (Dhairo, flower).

Methods of extraction and measurements are shown in Figure 1. Dye was extracted from each plant sample (crushed in powder form) by solvent extraction process in various solvents. Then the extract was separated from the residue by filtration. The solvent was removed from dye extract by evaporation at around 50°C. Then, 0.01 gm of solid extract (residue after removal of solvent) of each dye was re-dissolved in a desired solvent for recording absorbance-, fluorescence- and IR- spectra.

The absorbance and fluorescence of all the dye samples were measured on the Genesis-10 UV-Visible spectrophotometer and F93 Fluoro-Spectrophotometer in the wavelength of 300-900 nm. To identify probable chromophore groups present in a given natural dye, IR spectra were recorded with FT-IR spectroscopy (Shimadzu Corporation, IRPrestige21).

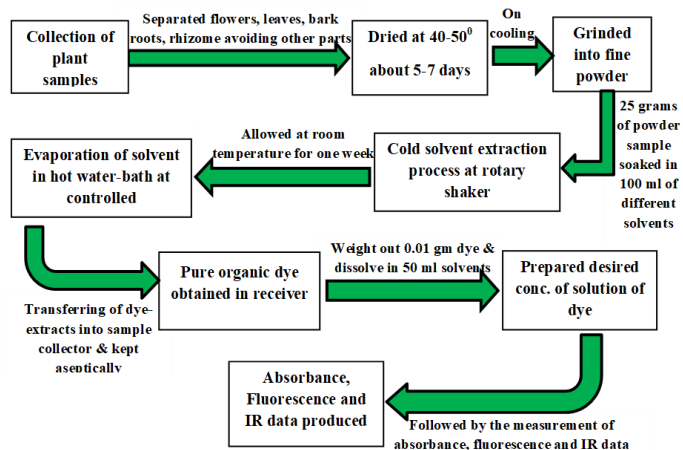


Figure 1. Schematic representation of the methods followed for the extraction of the natural dye and measurement of absorbance, fluorescence and IR spectra.

3. Results and discussion

The extracts obtained from a total of 15 plant samples by using cold solvent extraction method were re-dissolved in the same solvent in which they were originally extracted. The solutions were then used for investigation of their optical properties, in particular, absorbance, fluorescence, and transmittance (IR spectroscopy). The observed results are summarized in the following subsections.

3.1 Absorption of natural dye

Figure 2 shows UV-Vis absorption spectra as a function of radiation wavelength for all natural dyes. Among all the natural dye samples studied; *A. vasica* Nees and *M. esculenta* Buch Ham (in DDW), *R. arborium* L. and *N. arbor-tristis* L (in MeOH), *B. aristata* DC and *U. dioica* L (in EtOH), *B. aristata* DC, *U. dioica* L, *J. humile* L, *R. arborium* L., *O. wightiana* Wall, *C. coccinea* Wall, *A. vasica* Nees (Flower, in DDW), *R. anthopogon* D.Don and *W. fruticosa* L (in Acetone), *A. vasica* Nees, *A. vulgaris* L, *U. dioica* L, *J. humile* L, *N. arbor-tristis* L, *C. coccinea* Wall and *W. fruticosa* L (in DCM) and *A. vasica* Nees, *A. vulgaris* L, *U. dioica* L, *O. wightiana* Wall, *N. arbor-tristis* L and *W. fruticosa* L (in CH), exhibited a broad absorbance peak from wavelength (λ) ca. 300 nm (onset) – ca.500 nm (offset) and another additional sharp peak at ~650nm with FWHM of ca. 15 nm. Among all the analyzed samples, *A. vasica* Nees (in DDW), *N. arbor-tristis* L (in

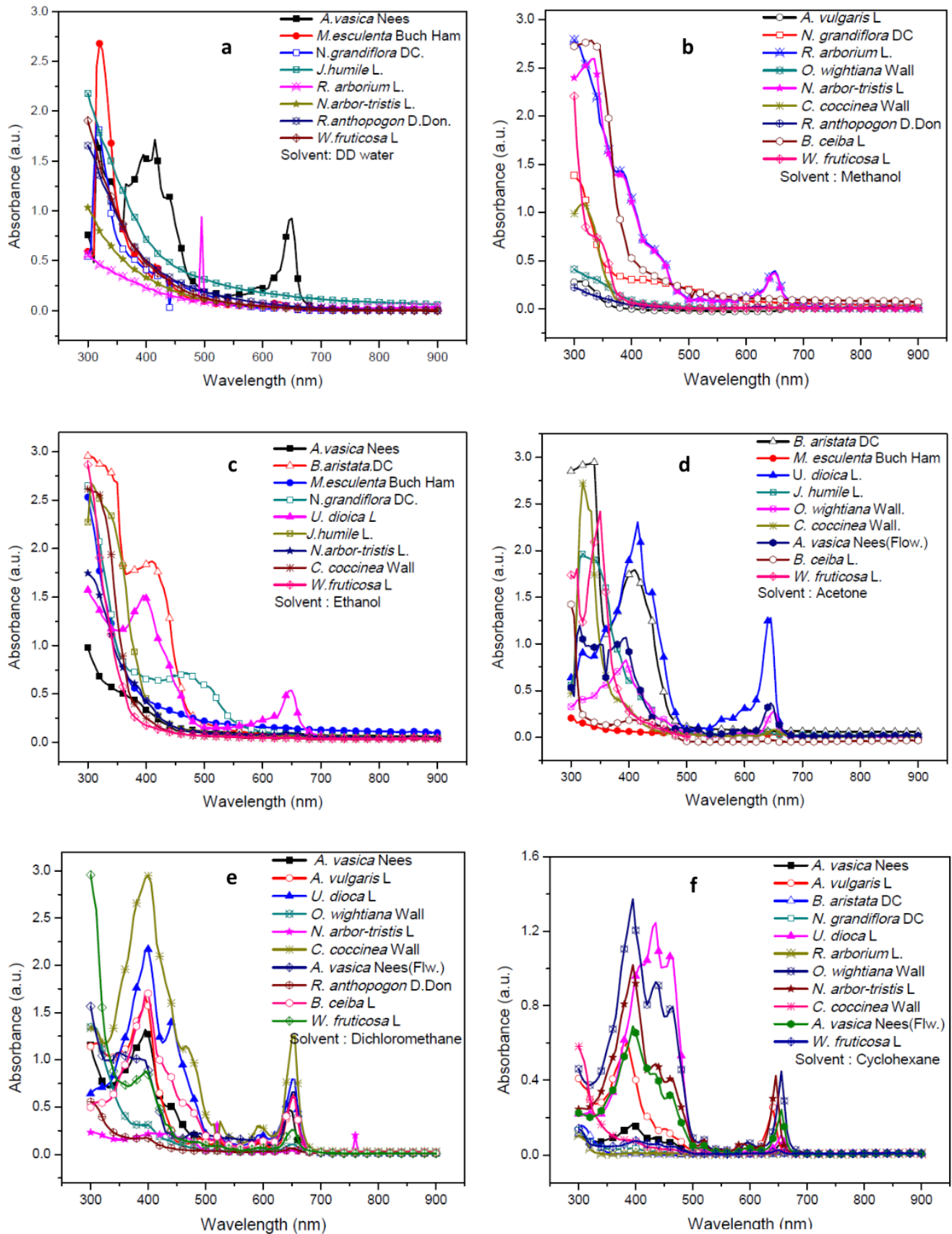


Figure 2 (a-f). Absorbance as a function of radiation wavelength for natural dye samples extracted in different solvents

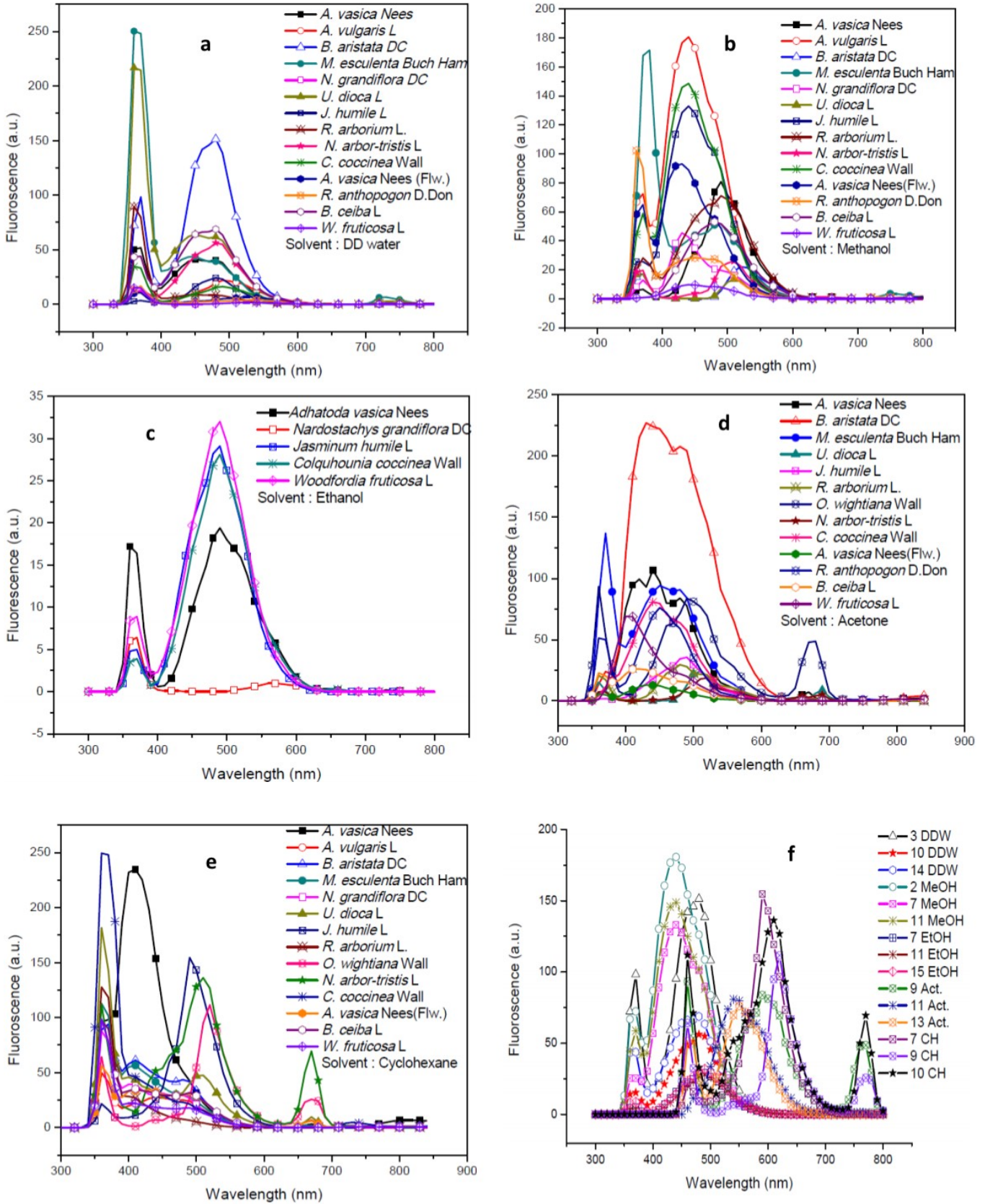


Figure 3 (a-e). Fluorescence spectra of various natural dye samples in different solvents as medium in the range of 300-800 nm wavelengths. Figure 3 (f) shows the best fluorescence spectra for some selective natural dyes in different solvents

MeOH), *U. dioica* L (in EtOH, Act, DCM and CH), *A. vasica* Nees (in act), *C. coccinea* Wall (in DCM) and *O. wightiana* Wall, *A. vasica* Nees (Flow., in CH) was found to exhibit better absorption in the UV-Vis spectrum of electromagnetic radiation. Remaining natural dye samples showed a monotonic decrease in the absorption for all the solvents studied, from wavelength (λ), 310 nm to 900 nm. In addition, when the polarity of the solvent increases, blue shift in the major peaks of each absorbance spectrum was noticed (Figure 2, a-f). This may be due to the effect of polarity of the solvent (as expected) or it may be due to the extraction of different molecule(s) with unique absorbance which was absent in that particular solvent.

The absorption maxima for dye extracts in the wavelength range ca. 400–500 nm may be attributed to absorption due to xanthophyll, flavone, carotene, and rhen molecules, respectively (Zhou *et al.*, 2011). Absorbance maxima observed at wavelength $\lambda = 411$ nm and $\lambda = 665$ nm (in cyclohexane) indicates the presence of either chlorophyll, anthocyanin or carotene or mixture of these compounds in the extract (i.e. these peaks may be due to absorption by individual species or may be attributed to the superposition of absorption peaks) since the natural dye generally contains either anthocyanin, chlorophyll carotenoids or mixture of them which have absorption peak at wavelengths 420 nm and 560 nm (Sari and Sunardi, 2011).

3.2 Fluorescence of plant extracts (natural dyes)

Figure 3 demonstrates fluorescence spectra, after excitation with 340 nm, as a function of emitted radiation wavelength for all the 15 natural dye extracts in various solvents. Fluorescence spectra indicated that emission heavily depends on the solvent, just as absorbance did. Almost all of the natural dyes extract exhibited fluorescence spectra at the excitation wavelengths of ca. 400 nm (onset) - 650 nm (offset) and the emission wavelengths of 640 nm – 700 nm, except for few dyes. It was very interesting to note that for a particular sample in the same solvent, fluorescent maxima with respect to absorbance maxima shifted by about 25 nm. For example, the absorbance maximum (λ_{max}) of the dye sample *A. vasica* Nees that appeared at about 400 nm (see in Figure 2(a)), is found to occur at 425 nm in the fluorescence spectrum (see in Figure 3(a)).

Again, a careful observation of Figure 3 (a-e) indicated that when polarity of the solvent was increased, the major peak of the fluorescence spectrum shifted towards blue side: for instance, the fluorescence peak of sample *N. arbor-tristis* L. (in cyclohexane, see in Figure 3 (e)) that appeared at ca.525 nm found to occur at ca. 500 nm in distilled water (see in Figure 3(a)).

Also, the Figure 3(f) represents the fluorescence spectra of some of the selected dye samples which showed good absorbance and emission in the visible or in the near-IR region of the solar spectrum. The selective samples and solvents used are *B. aristata* DC, *N. arbor-tristis* L, *B. ceiba* L (in DDW); *Artemisia vulgaris* L, *J. humile* L (in MeOH); *J. humile* L, *C. coccinea* Wall, *W. fruticosa* L (in EtOH) and *N. arbor-tristis* L, *R. anthopogon* D.Don (in CH). Thus, the prevalence of emissions in broad wavelengths range in between 400 nm to 800 nm (except only a small window at about 725 nm), of the natural dye samples may be useful for synthesizing organic light emitting diodes.

3.3 IR spectroscopy of natural dye

IR spectra recorded from natural dye samples; *A. vasica*, *A. vulgaris*, *B. artista*, *U. dioica*, *J. humile*, *R. arborium*, *O. wightiana*, *N. arbortritis*, *C. coccinea*, *A. vasica* flower and *R. anthopogon*, extracted in methanol, are presented in Figure 4(a-c) along with probable functional groups present in each sample. All the samples analyzed showed broad peak around 3300 cm^{-1} which is characteristic of stretching vibration of O-H bond. All three samples in Figure (4a) showed IR active in the peak positions at ca. 3326 cm^{-1} and ca. 2928 cm^{-1} which may be assigned to the bonded –OH and C-H stretching modes, respectively. Also, *A. vasica* and *U. dioica* showed IR active in the peak position at ca. 1628 cm^{-1} , which may be assigned to the bonded C=O stretching. Other probable functional groups are indicated in the figures themselves (see in Figure 4(b)). Similarly, *J. humile*, *R. arborium*, and *O. wightiana* showed IR active in the peak position at ca. 3301 cm^{-1} and 1607 cm^{-1} which may be assigned to the bonded –OH group and bending –NH group, respectively. All the three samples presented in Figure 4(c); showed IR active in the peak positions at ca. 3357 cm^{-1} and 1028 cm^{-1} which may be assigned to the bonded –OH and ester C-O modes, respectively.

4. Conclusion

From the UV-Vis-, fluorescence- and IR-spectroscopic investigation of natural dyes, it was observed that all the 15 samples exhibited a broad absorbance peak from wavelength λ , ca. 300 nm (onset) – ca.500 nm (offset) and another additional sharp peak at ~650nm with FWHM of ca. 15 nm. Moreover, among all the analyzed samples, *A. vasica* Nees, *N. arbor-tristis* L, *U. dioica* L, *A. vasica* Nees, *C. coccinea* Wall and *O. wightiana* Wall, *A. vasica* Nees found to exhibit fairly better absorption both in terms of intensity and broader wavelength range in the visible spectrum. Also, major peaks in absorbance spectrum shifted towards blue side

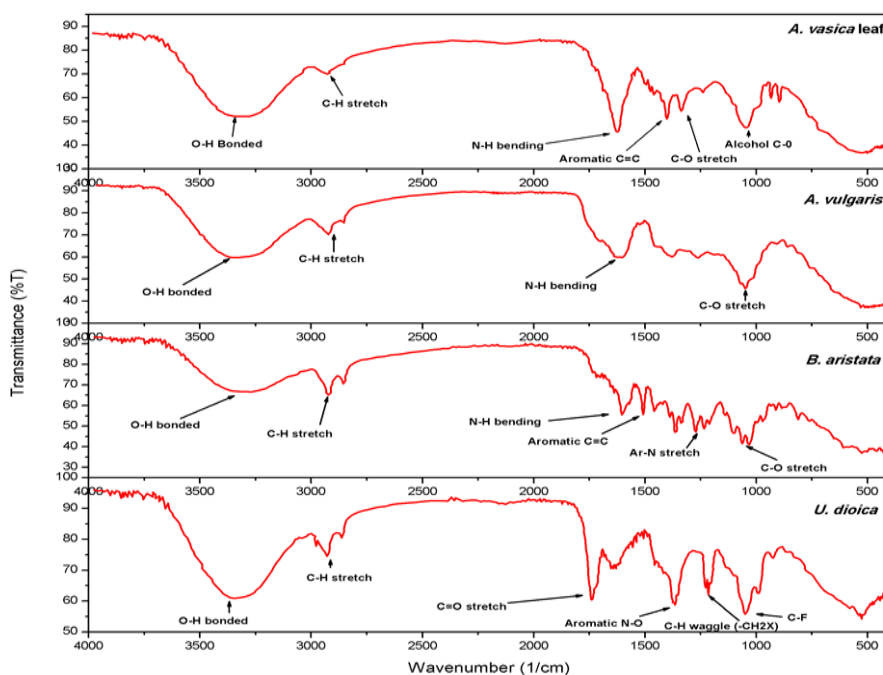


Figure 4(a). IR spectra recorded from natural dye samples; *A. vasica*, *A. vulgaris*, *B. aristata* and *U. dioica* extracted in methanol. All the three samples showed IR active in the peak positions at ca. 3326 cm^{-1} and 2928 cm^{-1} which may be assigned to the bonded -OH and C-H stretching modes, respectively. Also, *U. dioica* and *A. vasica* showed IR active in the peak position at ca. 1628 cm^{-1} , which may be assigned to the bonded C=O stretching. Other probable functional groups are shown in the figure itself.

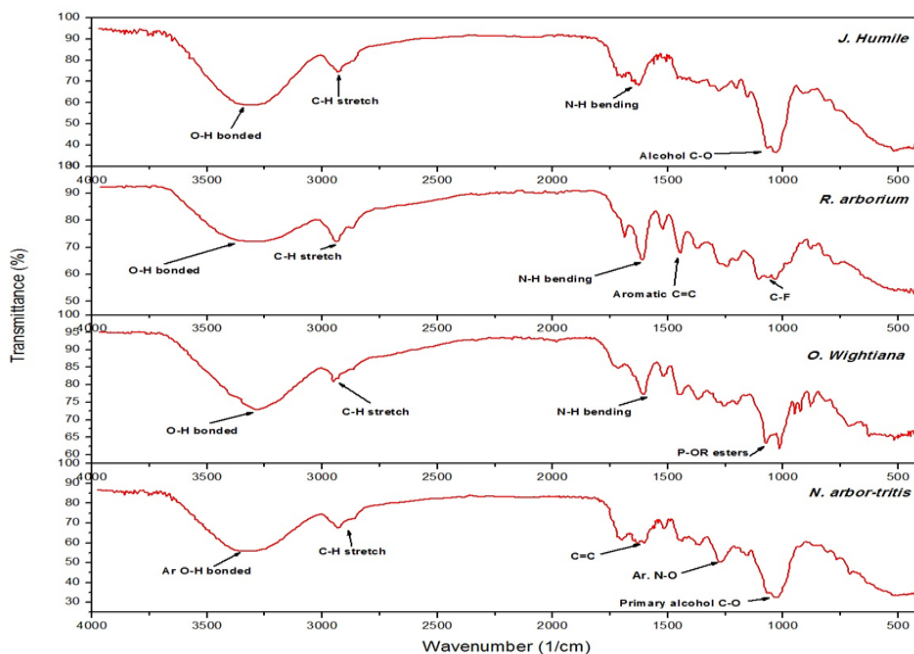


Figure 4 (b). IR spectra recorded from natural dye samples; *J. humile*, *R. arborium*, *O. wightiana* and *N. arbor-tritis* extracted in methanol. All the four samples showed IR active in the peak positions at ca. 2933 cm^{-1} which may be assigned to the C-H stretching modes. Similarly, *J. humile*, *R. arborium* and *O. wightiana* showed IR active in the peak position at ca. 3301 cm^{-1} and 1607 cm^{-1} which may be assigned to the bonded -OH group and bending -NH group respectively. Other probable functional groups are shown in the figure itself.

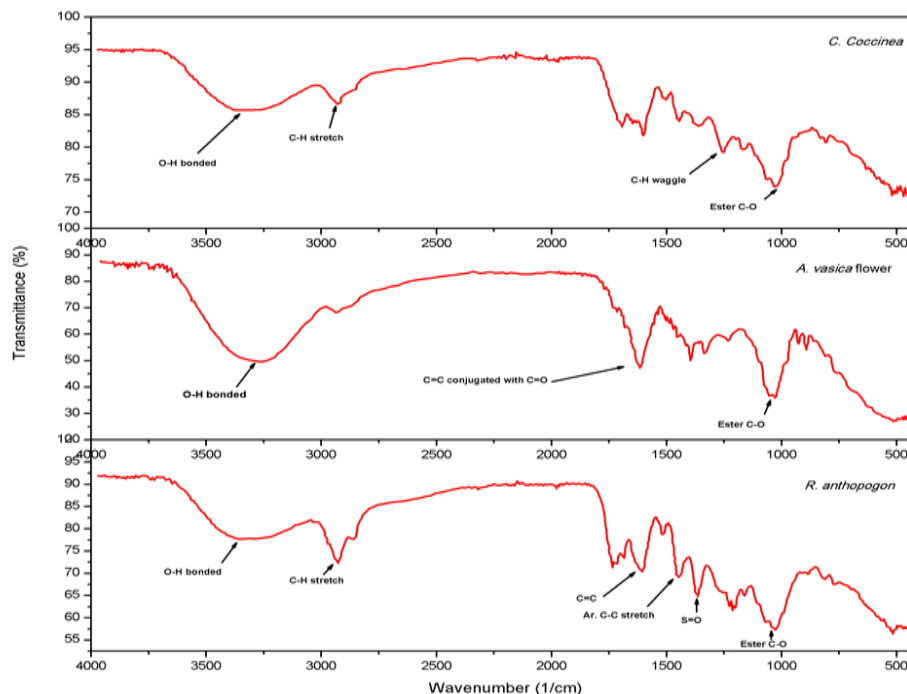


Figure 4 (c). IR spectra recorded from natural dye samples; *C. coccinea*, *A. vasica* flower and *R. anthopogon* extracted in methanol. All the three samples showed IR active in the peak positions at ca. 3357 cm^{-1} and 1028 cm^{-1} which may be assigned to the bonded -OH and ester C-O modes, respectively. Also, *A. vasica* flower and *R. anthopogon* showed IR active in the peak position at ca. 2929 cm^{-1} , which may be assigned to the -CH stretching. Other probable functional groups are shown in the figure itself.

when the polarity of the solvent increased. This may be due to the effect of the polarity of the solvent or it may be due to the extraction of different molecule (s) with unique absorbance which was (were) absent in a particular solvent.

Absorbance peak observed at wavelength $\lambda = 411\text{ nm}$ and $\lambda = 665\text{ nm}$ (in cyclohexane) indicated the presence of either chlorophyll, anthocyanin or carotene or mixture of these compounds in the extract. These peaks may due to absorption by individual species or the resulting peaks may be attributed to the superposition of the individual absorption peaks. Since the natural dye generally contains either anthocyanin, chlorophyll carotenoids or mixture of them which have absorption peaks at wavelengths 420 nm and 560 nm , exact identification of contributing species was not possible in our analysis of crude extract.

In summary, the prevalence of both the absorption and emissions in broad wavelength range from 400 nm to 800 nm (except only a small window at about 725 nm), by some selective samples, particularly by *B. aristata* DC, *N. arbor-tristis* L, *B. ceiba* L; *A. vulgaris* L, *J. humile* L; *C. coccinea* Wall, *W. fruticosa* L and *N. arbor-tristis* L, *R. anthopogon* D.Don, indicated that these samples may be useful for synthesizing OLEDs.

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