

# Spectral Characteristics of *Hibiscus sabdariffa* Organic Dye Used in Dye-Sensitized Photonics

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## Abstract

In this work, the spectral properties of the *Hibiscus sabdariffa* organic dye solved in different solvents were studied by introducing the effect of dye concentration on its absorbance and transmission spectra within the range 400-800nm. As well, the effect of adding acid to the dye solution on these properties was introduced. Results showed that the spectral properties of the dye depend substantially on the type of the solvent, which has to be chosen carefully to achieve the optimum properties of this dye to be used as a sunlight sensing organic medium in dye-sensitized solar cells. Also, the results showed that the spectral properties of this dye are noticeably affected by the presence of acid in the solution. Variation of acidic content in the dye solution was studied and its effect on both absorbance and transmittance was studied. As the acidic content in the solution was increased, the absorbance increased while transmittance decreased that may be attributed to dissociation of dye molecules, formation of new different compounds and/or quenching the spectral activity of the *Hibiscus sabdariffa* dye molecules.

**Keywords:** *Hibiscus sabdariffa*, Spectroscopy, Acidic environment, DSSC's

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## 1. Introduction

The *Hibiscus sabdariffa* dye (commercially known as Roselle) belongs to the family *Malvaceae* and is present in abundance through-out the world and has attained prominence as a jute substitute. Attempts are being made to extend its cultivation in areas which are not favorable for jute cultivation [1].

Water extract prepared from Roselle calyces is characterized by a brilliant red color and pleasant acid taste. Roselle extract is rich in anthocyanins, and could be used as a good source for producing a brilliant red colorant for many foods [2]. Anthocyanins, as with most natural food colorants, suffer from inherent instability [3]. Colour stability of anthocyanins depends on a combination of various factors including: structure of anthocyanins, pH, temperature, oxygen, and light and water activity. Enzymatic degradation and interactions with food components such as ascorbic acid, sugars, metal ions, sulfur dioxide and copigments are no less important [4].

It shows better mechanical properties when studied for injection-molded isotactic polypropylene/Roselle fiber composites [5] but still remains unexplored for its viability as substrate to grafting with vinyl monomers. The versatility of this magnificent chemical technique inspired the thoughts to implement it onto virgin *Hibiscus sabdariffa* stem fiber by using efficient methyl acrylate as principal monomer and explore its cumulative effect in binary vinyl monomer mixture with acrylic acid (AA), 2-vinyl pyridine (2-VP) and vinyl acetate (VA) as secondary monomer that remain unexplored, under the optimized conditions. The distinct properties such as swelling behavior, dye uptake behavior, moisture absorbance and chemical resistance were studied and the screening of these specific vinyl monomeric mixtures led to the development of novel graft copolymer that had physico-chemico-thermally modified properties [1]. The molecular structure of the anthocyanin is shown in Fig. (1) below.

Traditional fossil fuel energy sources are finite and release waste products into the atmosphere, such as  $\text{NO}_2$  and  $\text{CO}_2$ , that are detrimental to the earth's global environment. As a result, alternative energy sources are receiving increasing attention. Examples include wind, hydroelectric and solar power. In particular, solar power is attractive because the sun is the biggest energy source of the world. In 1991, O'Regan and Grätzel discovered a new type of solar cell which is called "dye-sensitized solar cell (DSSC)" [6]. DSSCs have attracted a great deal of interest as they offer high energy conversion efficiencies at low cost. Dye-sensitized solar cell based on electrochemistry at the interface between a dye adsorbed onto a porous network of nanometersized titanium dioxide particles and electrolyte. The components of dyesensitized solar cell are shown in Fig. (2).

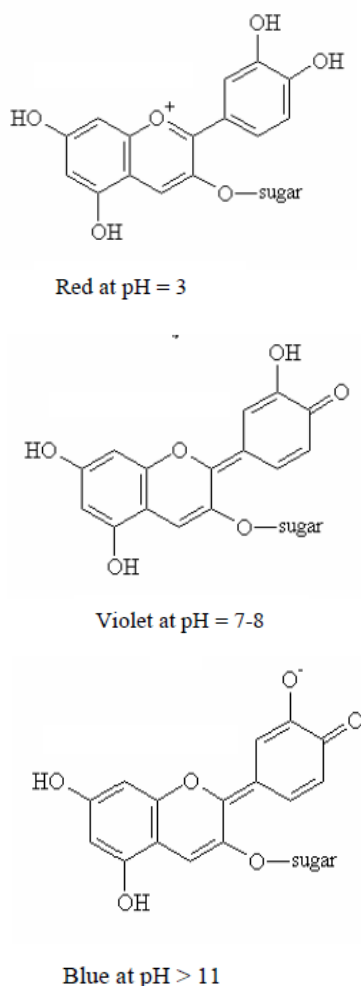


Fig. (1) Molecular structures of anthocyanin at various pH [6]

The *Hibiscus sabdariffa* dye solved in ethanol absorbs well in ultraviolet region of the electromagnetic spectrum and has good absorbance in the visible region but lower than that in UV

region. Consequently, this dye is good candidate for use in titanium dioxide dye-sensitized solar cells [6-9].

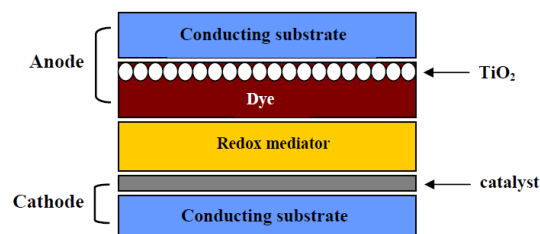


Fig. (2) The components of dye-sensitized solar cell [6]

In this work, the spectral properties of *Hibiscus sabdariffa* organic dye solved in different solvents (water, ethanol and acetone) were introduced and the effect of acidic environment hosting this dye was studied.

## 2. Experiment

In experimental part, the *Hibiscus sabdariffa* organic dye was prepared as fine powder the flowers of Roselle. The pure and clean flowers were carefully selected, crashed, milled and sieved to obtain as fine and homogenous powder as possible. Different samples were weighed and classified into three main groups according to their masses (M1, M2 and M3), where M1= 0.212 g; M2= 0.424 g; and M3= 0.636 g. Deionized distilled water, ethanol (99.9%) and pure acetone (98%) were used as solvents of the prepared dye samples due to the volumetric ratios between the dye powder and solvent. These solutions were placed in test tubes of good seal and kept at room temperature away from excess light to prevent any possible photochemical dissociation or thermal degradation.

The spectroscopic measurements (absorbance and transmittance) were carried out using UV-Visible spectrophotometer (SpectraAcademy SV-2100) operating in the wavelength range of 166-962nm with an optical resolution of about 2nm FWHM and a CCD detector with a resolution of 2048 pixels. This spectrophotometer could be connected to a personal computer in order to control the measurement process at high accuracy, high reliability and excellent reproducibility. The results presented in this work were averaged from consecutive readouts to achieve the reliability required for such analytical studies.

## 3. Results and Discussion

The experimental results of this work started from the determination of the range of wavelengths affected by the spectral properties of the *Hibiscus sabdariffa* organic dye solved in different solvents in

order to introduce both absorbance and transmittance peaks on the spectrum. Figure (3) shows the averaged absorption spectra of *Hibiscus sabdariffa* organic dye solved in water, ethanol and acetone within the wavelength range of 400-800nm. This study considered the spectral properties in this range of wavelengths (400-800nm) due to their importance when using such dyes in dye-sensitized solar cells. However, the spectral properties of this dye in ultraviolet region may be interested by other applications.

As shown in this figure, the values of absorbance of the three cases are slightly different; however, the fine analysis of these spectra explains that solving this dye in water makes it absorb better than that solved in acetone, while the dye solved in ethanol has lower absorbance than the former two. This result can be interpreted as follows.

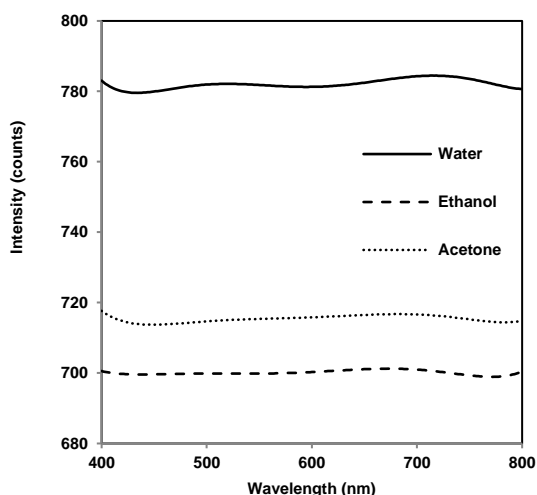


Fig. (3) Averaged absorbance spectra of the *Hibiscus sabdariffa* organic dye solved in different solvents within 400-800nm

Most properties of linear polymers are controlled by two different factors. The chemical constitution of the monomers determines the interaction strength between the chains, the interactions of the polymer with host molecules or with interfaces. The monomer structure also determines the possible local conformations of the polymer chain. This relationship between the molecular structure and any interaction with surrounding molecules is similar to that found for low-molecular-weight compounds. The second important parameter that controls polymer properties is the molecular weight [10]. Contrary to the situation for low-molecular-weight compounds, it plays a fundamental role in polymer behavior. It determines the slow-mode dynamics and the viscosity of polymers in solutions and in the melt. These properties are of utmost importance in

polymer rheology and condition their processability. The mechanical properties, solubility and miscibility of different polymers also depend on their molecular weights [11].

Due to the molecular structures of the dye and the three solvents, the presence of four hydroxide molecules in the molecular structure of the dye stimulates it to search for an excess of hydrogen to bond with. Such excess of hydrogen is provided by ethanol and acetone as they contain five and six hydrogen atoms, respectively, within the molecular structure of each of them, in contrast to water. This makes the reaction ability between the dye and ethanol or acetone higher than that between the dye and water, and hence more amount of the dye to solve in ethanol or acetone, which is normal [12-13]. As a result, such reaction decreases the concentration of the dye responsible to absorb the incident wavelengths and then the absorbance is decreased, as shown clearly in Fig. (4).

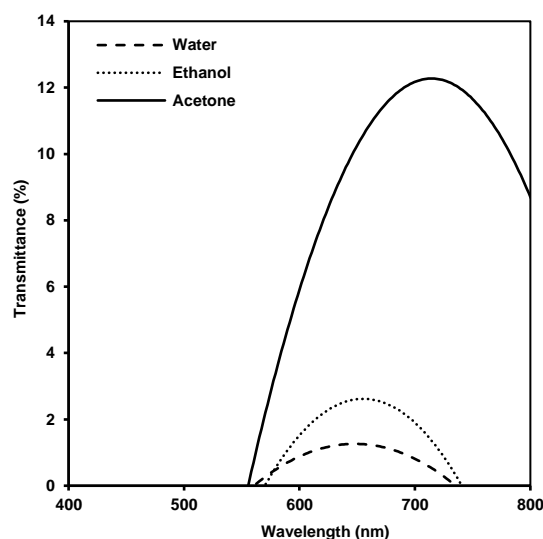


Fig. (4) Averaged transmittance spectra of the *Hibiscus sabdariffa* organic dye solved in different solvents within 400-800nm

Similarly, figure (4) shows the averaged transmittance spectra of *Hibiscus sabdariffa* organic dye solved in water, ethanol and acetone within the wavelength range of 400-800nm. It is observed, despite the low transmittance in general, that the sample solved in acetone has higher transmittance than those of water and ethanol. This is attributed to the pattern of the dye-acetone interaction, not towards quenching or extinction when compared with dye-water sample. While the dye-ethanol sample showed lower absorbance and transmittance than water and acetone due to the quenching effect imposed by ethanol on the spectral activity of *Hibiscus sabdariffa*, which is a general behavior of ethanol with similar organic compounds.

Accordingly, both samples of water and acetone were chosen to study the effect of acidic environment on the spectral properties of *Hibiscus sabdariffa* dye as a main goal of this study. From the bare observation of dye solubility in both solvents, the sample solved in acetone shows higher solubility than that solved in water. This is why we follow the work on samples solved in acetone only.

Figure (5) shows the absorbance spectra of *Hibiscus sabdariffa* dye solved in acetone at different concentrations in the spectral region 400-800nm. Starting from 550nm, the lower concentration (M1) shows lower absorbance than the other higher concentrations (M2 and M3) as the solvent (acetone) could solve much more amount of the dye and hence decrease the amount of dye to absorb the incident radiation. This is in accordance to Beer-Lambert law of absorption. The spectra shown in Fig. (5) are identical in shape, which may be considered as a characteristic feature for solving *Hibiscus sabdariffa* dye in acetone.

Though the absorbance of these concentrations is in general very low when considering large-scale analysis, such differences are of importance in quantum efficiency analysis of dye-sensitized solar cells. Also, such fine analysis is important when using such organic dyes in the quantum structures such as laser active media, photonic switches, etc.

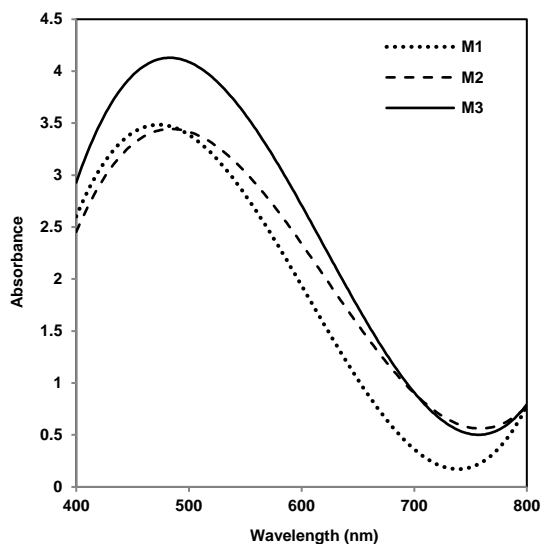


Fig. (5) Absorbance spectra of the *Hibiscus sabdariffa* dye solved in acetone at different concentrations

The presence of oxygen atom bonded to one of three carbon atoms in acetone molecular structure is an important factor to control the reaction of acetone with *Hibiscus sabdariffa* dye molecules towards the dissociation of these molecules and decreasing their concentration in the solution [10].

Figure (6) shows the effect of presence of acid in the solution of the *Hibiscus sabdariffa* dye in

acetone on the absorbance spectrum at a given concentration (M1). It is clear that the presence of acid decreases the absorption noticeably in the ranges 400-550nm and 650-800nm while both curves are close to each other in between these ranges (550-650nm). Acidic environment supports the solubility of the dye in the solvent leading to decrease the absorbing amount of the sample.

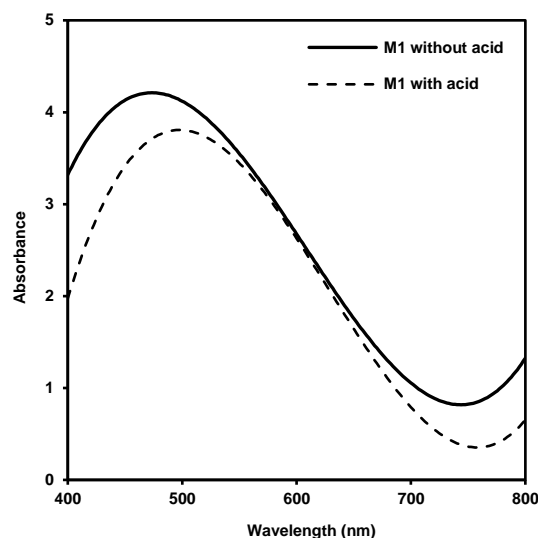


Fig. (6) Effect of presence of acid in the solution of the *Hibiscus sabdariffa* dye in acetone on the absorbance spectrum at a given concentration (M1)

Knowing that Roselle plant inherently contains some acidic components, the acidic environment is degrading the absorbance of *Hibiscus sabdariffa* dye, so, avoiding any increase in the pH of the surrounding environment is important for this dye to absorb in the visible region of electromagnetic spectrum as the acidic components are contributing to the characteristic spectral properties of this dye.

Increasing the concentration of the dye solved in acetone to M3, as shown in Fig. (7), a slightly different behavior is observed as the effect of adding acid to the solution is not high enough to change the absorbance at the region below 550nm, while reasonable decrease is observed later in presence of acid in the solution. This is attributed to increasing the solubility of the dye in the acidic environment and hence decreasing the amount of dye to absorb the incident radiation.

In order to determine the effect of acidic environment precisely, the absorbance and transmittance spectra of the *Hibiscus sabdariffa* dye solved in acetone at a given concentration (M3) and different concentrations of the acidic content in the solution, as shown in Fig. (8) and (9).

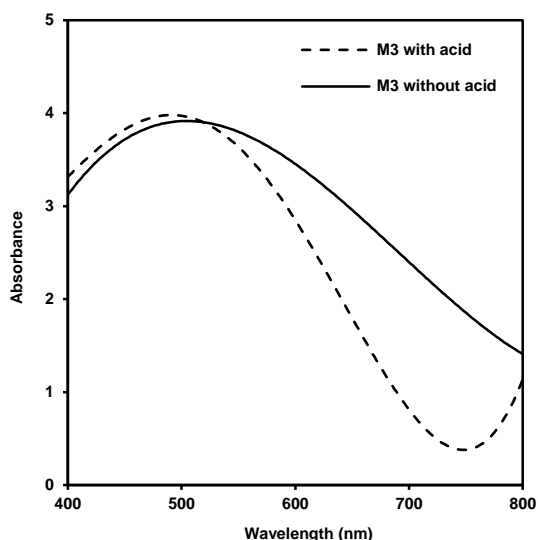


Fig. (7) Effect of presence of acid in the solution of the *Hibiscus sabdariffa* dye in acetone on the absorbance spectrum at a given concentration (M3)

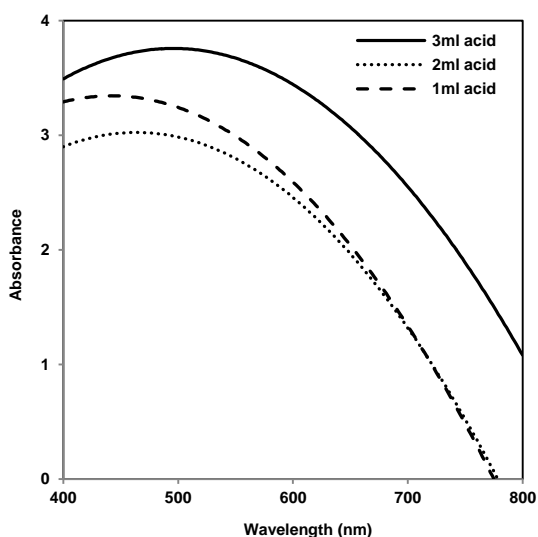


Fig. (8) Absorbance spectra of the *Hibiscus sabdariffa* dye solved in acetone at a given concentration (M3) and different concentrations of the acidic content in the solution

The effect of acidic environment shown in Fig. (8) on the absorbance of the dye solved in acetone was discussed earlier. The effect of acidic environment on the transmittance is reasonably observed in Fig. (9) as the transmittance of the dye solution with 3ml acid was decreased to about 10% of its values with 1ml and 2ml. This effect is not attributed only to the decrease in the amount of *Hibiscus sabdariffa* dye but also to the formation of a new compound that compete to absorb in the same spectral region. One can note some contradiction with the behaviors presented in Fig. (6) and (7), however, no real contradiction exists since figures (6) and (7) show the effect in case of absence and

presence of the acid in the solution regardless its concentration, while figures (8) and (9) show the effect of acid concentration at fine variation, which is very important in accurate analysis of such photonic media.

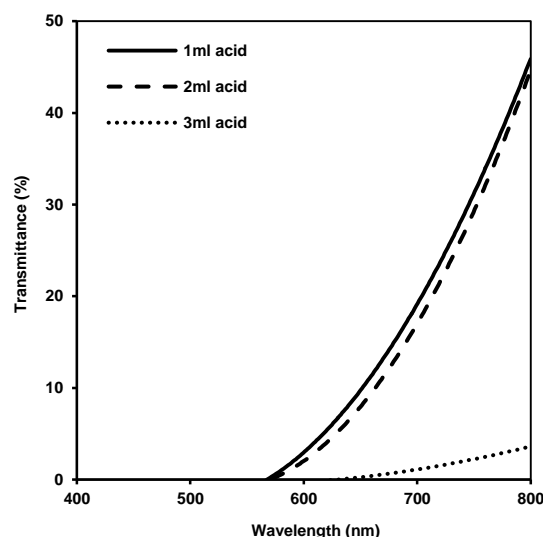


Fig. (9) Transmittance spectra of the *Hibiscus sabdariffa* dye solved in acetone at a given concentration (M3) and different concentrations of the acidic content in the solution

#### 4. Conclusion

From the results presented in this work, we could conclude that the acidic environment of the *Hibiscus sabdariffa* dye solved in acetone has an important effect on the spectral properties of such dye. Adding acid to the dye solution caused to decrease its absorbance in the range 400-800nm and noticeable decrease was shown in the range 550-700nm when the concentration of the dye got higher. The effect of acidic environment was fundamentally observed at higher concentrations of the added acid to the dye solution since the absorbance was shifted upward and the transmittance was decreased.

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