SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF AZO DYES DERIVED FROM SULPHANILIC ACID

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Abstract

Azo dyes were synthesized using sulphanilic acid as the diazo component and betaoxynaphthoic acid (BON acid) and 1-naptholas the coupling components,the wavelength of maximum absorbtion is at 471.00 and 509.00 nm on the solvent ethanol for dye 1 and dye2respectively.thus the synthesized dyes were characterized using Gallan kamp melting point apparatus in which dye 1 and dye 2 have the melting point range of $298- 200\,°C\ respectively.\ Fourier\ transform\ infrared\ spectroscopy$ studies shows that dye 1 has the following functional group and vibrational frequencies;3429.2 cm^{-1} NH-stretch,2981.9 cm^{-1} CH-stretch,1722.0 cm^{-1},1677.3 cm^{-1} N=N stretch.While dye 2 has the following;1722.0 cm^{-1} NH-stretch,2881.9 cm^{-1} CH-stretch,1722.0 cm^{-1} ,1677.0 cm^{-1} N=N stretch. The electrical conductivity was varied from 10-10,000 Hz and the electrical conductivity at power frequency of 60 Hz was obtained to be 1.36×10^{-2} and 9.81×10^{-6} S/m for dye 1 and dye 2 respectively. The electrical conductivity of the two azo dyes comes within the range of the semiconductor band of $10^{2} - 10^{-12}$S/cm.

1.0 INTRODUCTION

Dyes are organic colour compounds which contains groups such as -N=N (azo group), -C=O (carbonyl group), (nitro) -NO, etc. and auxochromic group such as amino and substituted amino groups. In other words dyes are organic colored substance that chemically bonds to the substrate to which it is being applied, this distinguish dyes from pigments which do not chemically bind to the material they color. The dye is generally in an aqueous solution and may require a mordant to improve the fatness of the dye on the fiber. Both dyes and pigment are colored, because they absorb only some wavelength of visible light. Dyes are usually soluble in water whereas pigments are insoluble. The first synthetic dye mauve was discovered serendipitously by William Henry Perkin in 1856. The discovery of Mauveine started a surge in synthetic dyes and in organic chemistry in general. Other aniline dyes followed, such as fuchsine, safranine and induline and many thousands of synthetic dyes have since been prepared. The color of a dye is dependent upon the ability of the ability of the substance to absorb light within the visible region in the electromagnetic spectrum (400-700nm). An earlier theory known as Witt theory states that a colored dye has two components, a chromophore which imparts colour by absorbing light in the visible region (some examples are nitro, azoquinoids groups) and an auxochrome which serves to deepen the color. These theory has been suspended by modern electronic structure theory has been suspended by modern electronic structure theory which states that the colour in dyes is due to excitation of valence-electrons by visible light. (Gupta, 2009).

Dyes are aromatic compounds that absorb light of wavelength ranging between 700 – 350 nm. The colors of these dyes are originated by absorbing the light in the visible region of the spectrum due to the delocalization of *n*- and π-electrons throughout their structures (Aziz et al., 2009). The difference between semiconducting and good

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conducting materials is that the resistance of the good conductors declines rapidly as the temperature drops off, whereas the resistance of semiconductors increases notably as the temperature falls down to the absolute zero. The structure of the semiconductors tolerates electrical current to pass through and they possess electrical resistivity ranging from 10^{-2} to 10^{9} Ω.cm at room temperature. The d.c. electric conductivity of azo dyes has been investigated by a number of research groups. (El Wahed et al., 1994)

## 2.0   MATERIALSANDMETHODS
2.1   Materials

Weighing balance, beaker, measuring cylinder (10 cm3). Thermometer, funnel, melting point instrument, UV-visible spectrophotometer, round bottom flask, glass rod, spatula, boiling tube and Fourier transformed infrared (FT- IR) spectrophotometer, methanol, distilled water, sodium nitrite, hydrochloride acid, ice block, Betaoxynaphtoic acid (BON acid, and sulphanilic acid.

2.2 Procedure

2.2.1 Diazotization of the sulphanilic acid

Sulphanilic acid (4.0g, 1 mol) was dissolved in 50 ml of NaOH. The solution was then cooled in an ice bath. A solution of sodium nitrite (50 ml, 1 mol) and 10 ml concentrated HCl was added drop –wise with continous stirring for 30 minutes to form the diazonium salt. As shown in the reaction below.
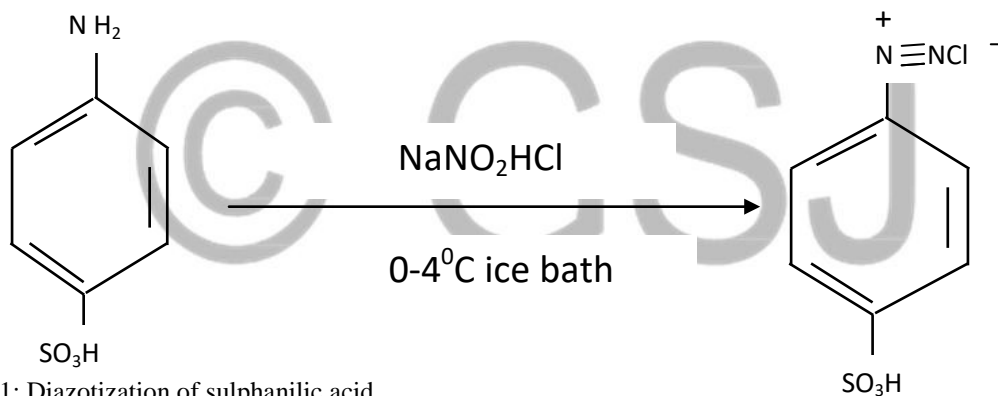
Scheme: 1: Diazotization of sulphanilic acid

3.2.2 Coupling reaction with betaoxynaphtoic acid (BON acid)

Coupling reaction was carried out with betaoxynaphtoic acid and was added drop wise to the diazonium salt of sulphanilic acid in the ice bath. The mixture was stirred vigorously for a hour and left over night after which it was filtered, recrystallization and stored in refrigerator.
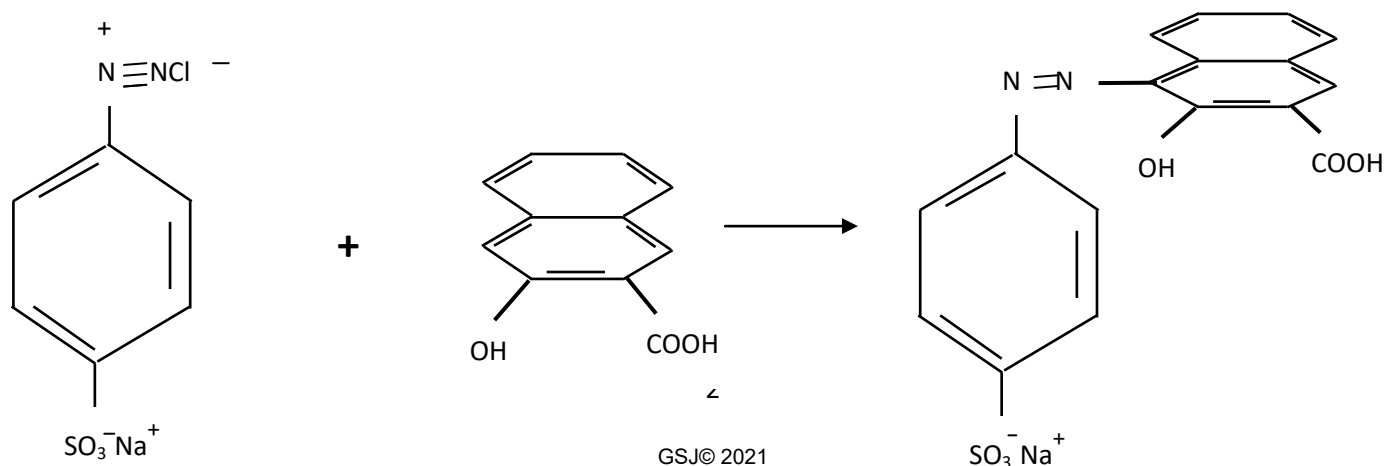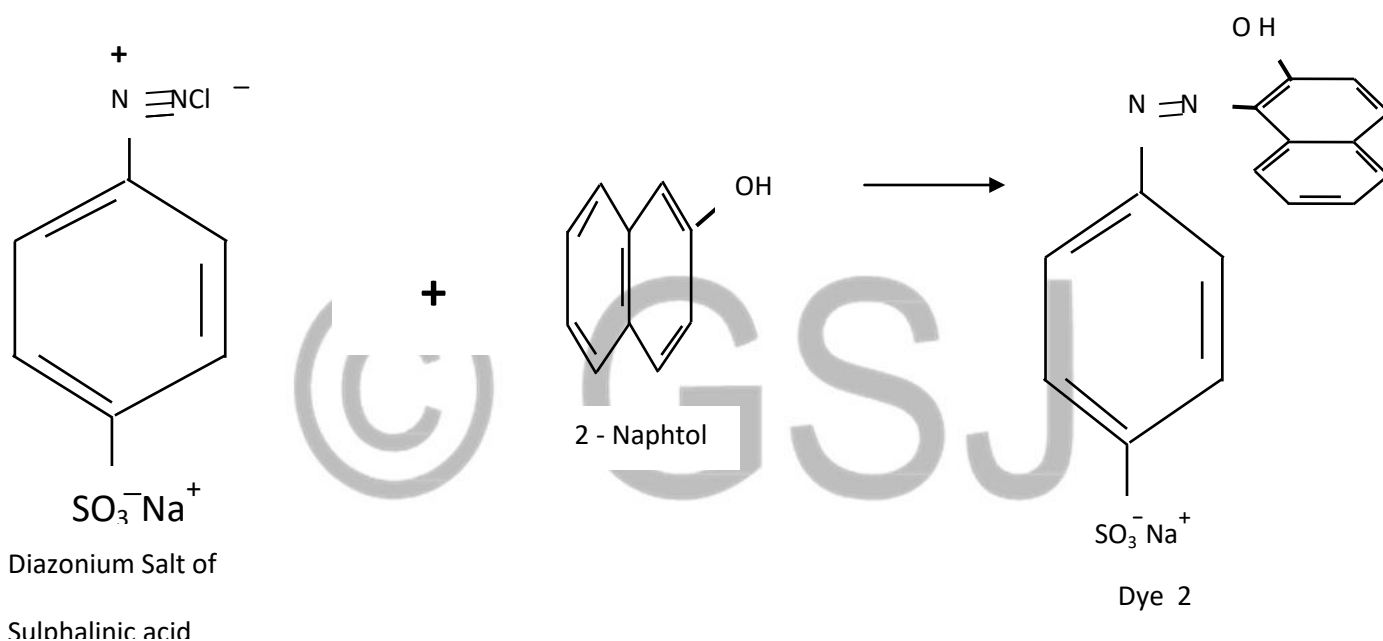
Jkk   Betaoxynaphtoic acid   Dye 1

Scheme.2: Diazonium salt reacting with betaoxynaphtoic acid

3.2.2.1 Coupling with 2-naphtol

In a test tube 0.8 ml of diazomium salt was thoroughly mixed with 2-naphtol. The precipitate of the dye was filtered and allowed to dry at room temperature. As shown below:

Diazonium Salt of

Sulphalinic acid

2 - Naphtol

Dye 2

Scheme 3 : Coupling with 2-naphtol

2.2.3 Melting point determination

The melting point was determined by the open capillary method and will be expressed in ℃. The dyes will be determined using gave ncanp. Electrothermal melting point apparatus.

2.2.4 Determination of visible absorption spectroscopy

Visible absorption spectra was recorded on ethanol and DMSO (Jen way UV/visible spectrophotometer, model: 6405) by (Dudley and Lan, 1980)

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2.2.5 Fourier transforms infrared spectroscopy Pelkin Elmer spectrum 100 (FT-IR)

The infrared spectra of the dyes were determined using the FT-IR spectrophotometer to determine the functional groups present.

2.6 Electrical Conductivity

The electrical conductivity measurements were obtained by employing a standard process of (Bekkali, *et al*., 2004). A known amount of sample was pressed into pellets using a Carver Laboratory press. These pellets were then utilized for the measurement of the conductivity of the materials. The thickness and diameter of the sample pallet were measured using a micrometer screw guage. The pellet thickness of about 2.45mm and the sample cell diameter of about 3.89cm were held constant for the electrical resistance measurement at a frequency range of 200-100000Hz using a programmable LCR meter and the result obtained was used to calculate the electrical conductivity of the samples using the relation below:

σ = l/ RA. Where σ is the electrical conductivity, l is the thickness of the dye pellet (l = 2.45mm), R is the electrical resistance of the dye pallet and A is the cross-sectional area of the dyes.

But $A = \pi r^2$ where r is the radius of sample pellet obtained from the diameter of the sample pellet

(i.e r = d/2) but d = 3.89cm hence r = 1.945cm.Hence :

A = 3.142 x (1.945 x 10^{-2})^2

A=1.1886 x 10^{-3}m^2

Therefore: σ = 2.45x 10^{-3}/R (1.1886 x 10^{-3}), where R is the resistance value of the synthesized compound measured at different frequency using LCR-meter

3.0 RESULTS

TABLE 1.0: Physical Properties of the Synthesized Dyes

S/N	sample	Melting Points °C	Colour
1	Dye 1	297-298	Purple
2	Dye 2	198-200	Orange

The melting point was determined using gallan kamp melting point apparatus in which dye 1 is having a melting point range of 297 -298℃ and dye 2 is having a melting point of range of 198 ℃ -200℃.Thus, dye 1 has the highest melting point simply because of its molecular weight. The closeness in range of the melting point indicates the purity of the synthesized compound dye. This is shown in table 4.1

Table.2: Wavelenght of maximum absorption (λmax (nm))

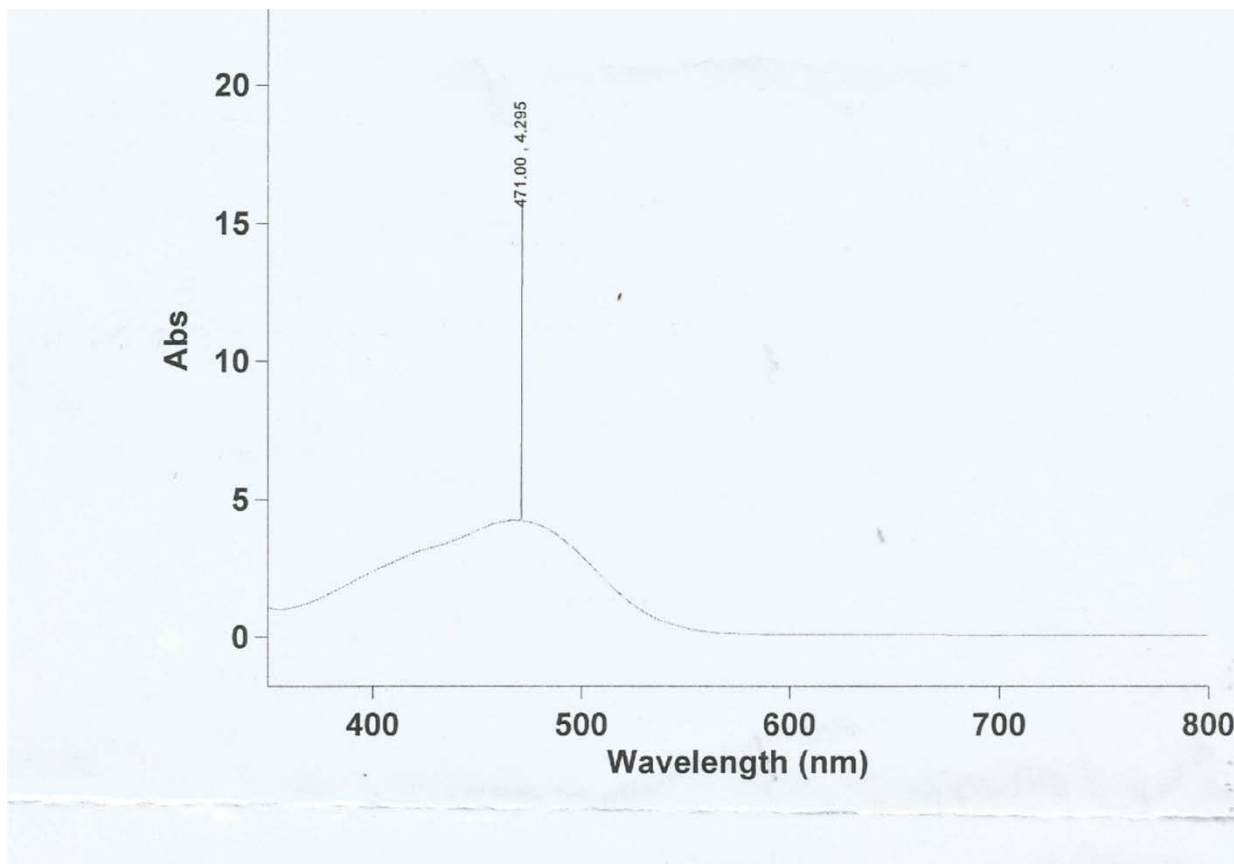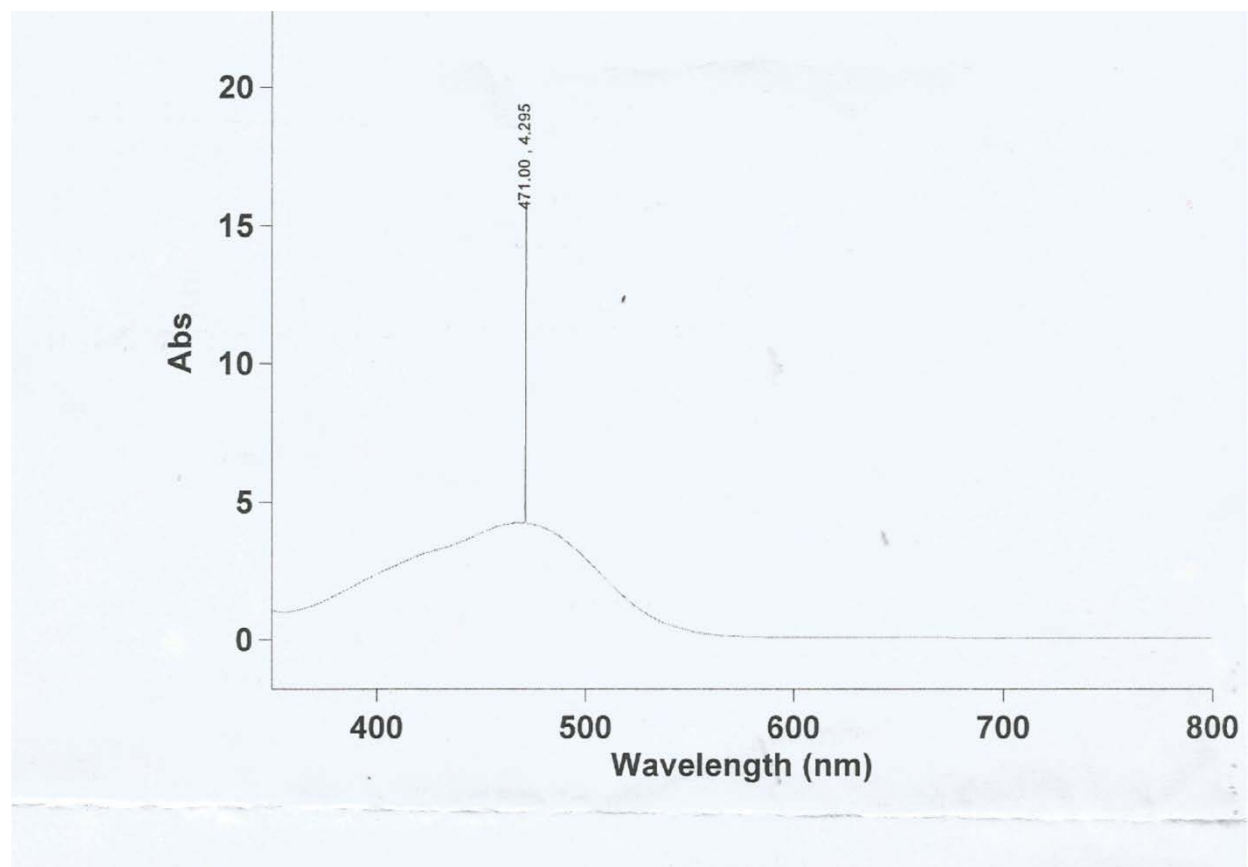| S/N	Sample	Ethanol
1	Dye 1	471.00
2	Dye 2	509.00

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Fig 1: Wavelength of Dye 1

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Fig 2 Wavelength of Dye 2

Uv-visible spectra indicated the maximum absorption level for dye 1 and 2 within the range of 471.00 nm and 509.00 nm for ethanol solvent respectively. Dye 2 happens to have the highest wavelength of maximum absorption respectively. This is shown in Table 4.2

Table 3: IR-vibrational Frequencies of the Synthesized Dyes

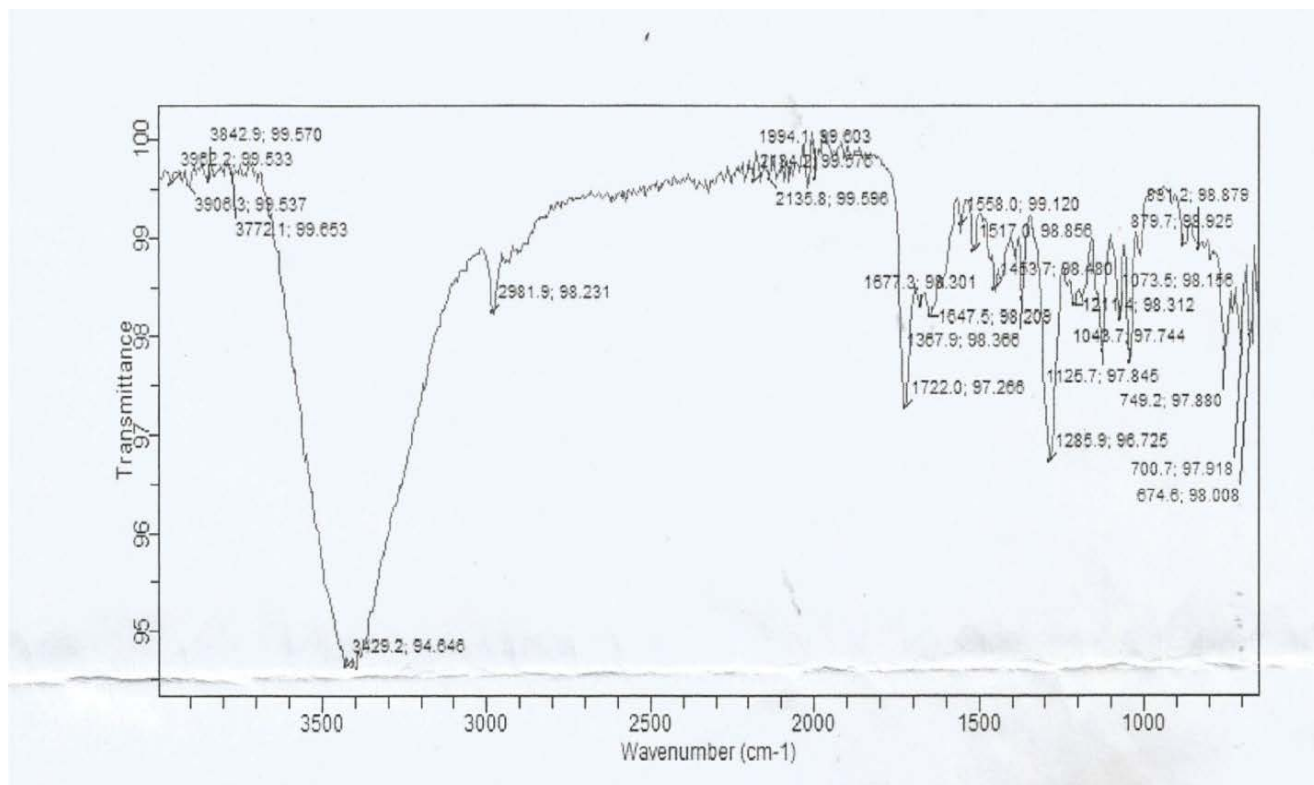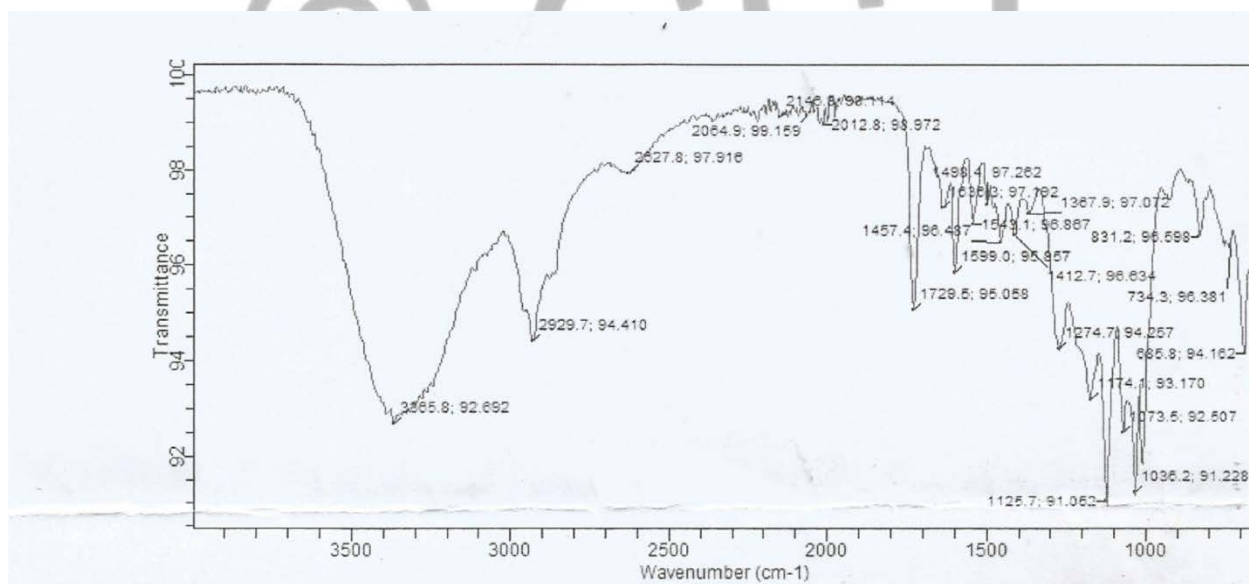| Dyes	IR Vmax (cm^{-1})
1	3429.2 (NH-Stretch), 2981.9 (CH-Stretch), 1722.0, 1677.3 cm^{-1} (N=N)
2	3429.2 cm^{-1} (NH-Stretch), 2881.9 (CH-Stretch), 1722.0, 1677.3 (N=N)

Fig 3: FT-IR spectrum of Dye 1

Fig: 4: FT-IR spectrum of Dye 2

The FT-IR is to determine the functional group and vibrational frequency present in the sample as shown in table 4.3. The results shows the functional group and the vibrational frequency present in the synthesized dyes shown; 3429.2 (NH-Stretch), 2981.9 (CH-Stretch), 1722.0, 1677.3 cm^{-1} (N=N) stretch vibrations for dye 1

Dye 2 is 3429.2 cm^{-1} (NH-Stretch), 2881.9 (CH-Stretch), 1722.0, 1677.3 (N=N) bending vibration respectively.

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TABLE 4: ELECTRICAL CONDUCTIVITY OF SYNTHESIZED DYES AT 60 Hz

DYES	Electrical conductivity (S/m)
1	1.36E-02
2	9.81E-06

4.0 Discussion

Dye 1 and 2 were synthesized from the reaction of the diazonium salts of sulphalinic acid with betaoxynapthoic acid (BON acid), and β-napthor as the coupling components. The colour of the dye span from purple to orange. Thus the electrical conductivity was carried out using standard methods of (Bekkali, *et al*., 2004) with the use of programmable LCR meter. The electrical conductivity was varied from 10-10,000 Hz and the electrical conductivity at power frequency of 60 Hz was obtained to be 1.36×10^{-2} and 9.81×10^{-6} S/m for dye 1 and dye 2 respectively. The electrical conductivity of the two azo dyes comes within the range of the semiconductor band of $10^2 - 10^{-12}$ S/cm. It was observed that Dye 1 possesses relatively greater reorganization of energy, higher electronic coupling, and hence greater electron transfer mobility as could be seen in their higher electrical conductivity value obtained from the result in Table 4.0, which means that Dye 1 can be more ideal candidate as a high performance n-type organic semiconductor material (Palilis *et al*., 2003). The higher the electron mobility the higher the electrical conductivity. Skotheim *et al*., (1998). Thus the increase in the electrical conductivity could also be attributed to the presence of the anchoring group in the coupling component which further triggered the delocalization of the electrons in the molecules (Nirmala *et al*., 2015) .

4.1 Conclusion

Azo dyes were synthesized using Betaoxynaphthoic acid (BON ACID) and 1-naphtol as the coupling components, the wavelength of maximum absorption were at 471.00 and 509.00 nm on the solvent ethanol for both dye 1 and 2. FT-IR spectroscopy gives the functional group present in each of the dye. The electrical conductivity was varied from 10-10,000 Hz and the electrical conductivity at power frequency of 60 Hz was obtained to be 1.36×10^{-2} and 9.81×10^{-6} S/m for dye 1 and dye 2 respectively. The electrical conductivity of the two azo dyes comes within the range of the semiconductor band of $10^2 - 10^{-12}$ S/cm.

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