



SYNTHESIS, CHARACTERIZATION AND ELECTRICAL CONDUCTIVITY OF AZO DYES DERIVED FROM 4-METHYLANILINE AS THE DIAZO COMPONENT USING N, N-DIMETHYLANILINE AND BETA-HYDROXYNAPHTHIONIC ACID (BON ACID) AS THE COUPLING AGENTS

***Obadahun j, Richard. A Oladimeji, Blessing. I Samuel**

Department of Science and Laboratory Technology,

**Directorate of Science Technology, Nigerian Institute Of Leather And Science Technology (NILEST),
Samaru Zaria, Kaduna State, Nigeria.**

***Correspondence Author: E-mail: joshuaobadahun@gmail.com; GSM: +2348067280257**

ABSTRACT

Azo dyes were synthesized via diazotization and coupling reaction using 4-methylaniline as the diazo component, Bon Acid and N, N-dimethylaniline as the coupling component, where the wavelength of maximum absorption is at 358.00 nm on the solvent Ethanol, and 444.00 nm on the solvent DMSO for dye A While 390.00 nm on the solvent Ethanol, and 455.00 nm on the solvent DMSO for dye B. FT-IR spectroscopy studies shows that dye A has the following functional group and Vibrational frequencies; 3362.1 cm^{-1} NH Stretch, 2914.8 cm^{-1} CH - stretch, 1654.9 cm^{-1} , 15804 cm^{-1} , 1543.1 cm^{-1} N=N stretch. While dye B has the following; 3276.2 cm^{-1} , OH- stretch, 2814.1 cm^{-1} CH-stretch, 1654.9 cm^{-1} , 1625.1 cm^{-1} , 1513.3 cm^{-1} N=N Stretch. The electrical conductivity of the synthesized dyes were observed to be within the range of 10^{-6} - 10^{-9} S m^{-1} . The electrical conductivity of the dyes lies within the range of electrical conductivity for semiconductor which is between 10^{-12} - 10^2 S m^{-1} (Aziz et al., 2002). However, Dye B was observed to have the highest electrical conductivity of 2.61×10^{-6} S m^{-1} at 60 Hz. This can be attributed to the fact that dye B have continuous conjugation due to the presence of betahydroxynaphthionic acid and hence have higher electrical conductivity.

INTRODUCTION

Dyes are coloured organic substance which binds to material and imparts colour to the material. The colour of a dye is due to the presence of a chromophoric group. They are widely used to colour the substrate like textile fibre, paper, leather, hair, fur, plastic material, wax, a cosmetic base and food stuff. (Mesitah, 2008). Based on chemical structure of chromophore, there are 20-30 different groups of dyes. However, Azoe.g (Monoazo, Diazo, Triazo, Polyazo) anthraquinone, phthalocyanine and triarylmethane dye are the most important groups (Safwat,

2005). These colors are originated from absorbing light in the visible region of the spectrum, making use of the delocalization of n - and π -electrons throughout their structures

The majority of industrial important azo dyes belong to the following classes: Acid dyes, basic dyes, direct dyes, mordant dyes, reactive azo dyes are ionic dyes (Anliker *et al.*, 1981) dyes contain at least one Nitrogen- Nitrogen (N=N) double bond, however, many different structures exist, for example, in the azo dyes, monoazo dyes have only one (N=N) double bond, while diazo and triazo dyes contain two and three (N=N) double bonds respectively.

The azo groups are generally connected to benzene and naphthalene rings. These side groups, are necessary for imparting the colour of dye, with many different shades and intensities (Zollinger1991).

Azo dye are the largest class of synthetic aromatic dyes composed with one or more (-N=N-) groups and sulfonic (-SO₃) group with a lot of commercial interest (Vandevere *et al.*, 1998). Azo dyes are water-soluble synthetic organic compound. Generally, azo dyes usually contain; one, two or three azo linkages, linking phenyl, naphthalene rings that are usually substituted with some functional groups including triazine amine, chloro, hydroxyl, methyl, nitro, and sulphonate(Bell *et al.*, 2000). There are more than 3000 azo dyes which includes Astazon Red GTLN, Maxilon Blue GRL, and sandolan yellow, cosmetics, food colouring and paper production industries (Lorimer *et al.*, 2001; Elbanna *et al.*, 2010). About 80% of azo dyes are used in the dyeing process of textile industries. It had been estimated that approximately 10% of the dyes used in dyeing process do not bind to the fibre and are released into the environment. Nowadays around 10 thousand of these azo couples are described and more than two thousands are applied to colour various materials. (Asad, *et al.*, 2007). The main difference between semiconductors and good conductors is that the resistance of the latter declines rapidly as the temperature decreases, whereas the resistance of semiconductors increases remarkably as the temperature falls down to the absolute zero (Salih, 2012). The structure of the semiconductors allows electrical current to pass through and they possess electrical resistivity ranging between 10⁻² Ω·cm and 10⁹ Ω·cm at room temperature. The d.c. electric conductivity of azo dyes has been investigated (Abd El Wahed, 1994). The factors that are affecting the electric conductivity have been intensively studied by a number of research groups (Halliday, 2005).

MATERIALS AND METHODOLOGY

Materials

Sodium hydroxide, Hydrochloric acid, Methylaniline, DMSO, Distilled Water, N,N-dimethylaniline, Sodium Nitrite, acetic acid, BON Acid. Beaker, Filter papers, Thermometers, Measuring Cylinder, weighing balance, Funnel, Wash Bottles, UV-Visible Spectrophotometer, round bottom flask, Spatula, Stirrer, Gallankamp Melting Point, Carver Laboratory press, programmable LCR meter.

Methodology

Diazotization of 4-methylaniline

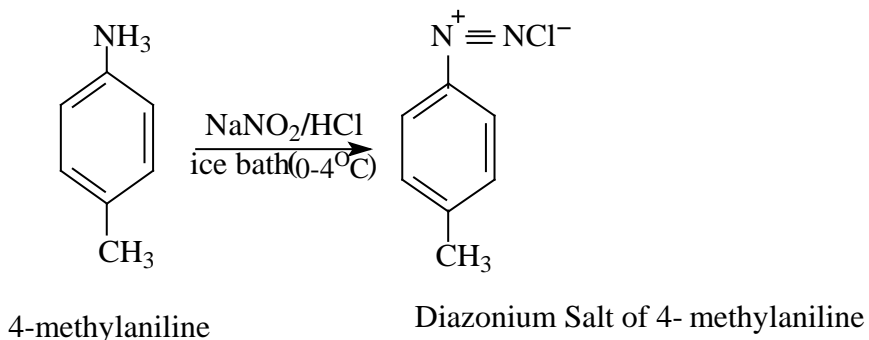
Diazotization of 4-methylaniline was dissolved in warm mixture of concentrated Hydrochloric acid (20 cm³).

The Solution was then Immersed in an ice bath and cooled to 0-4 °C with Vigorous Stirring. Sodium Nitrite (3.7 g, 0.054 mole) was dissolved in water (10 cm³) and the Solution was added slowly with stirring and tested with potassium iodide starch paper which was turn blue-black.

The Temperature was maintained below 4 °C to avoid Decomposition of the Diazonium salt throughout the preparation as Shown below;

Synthesis of the Dye

Diazotization of the 4-methylaniline

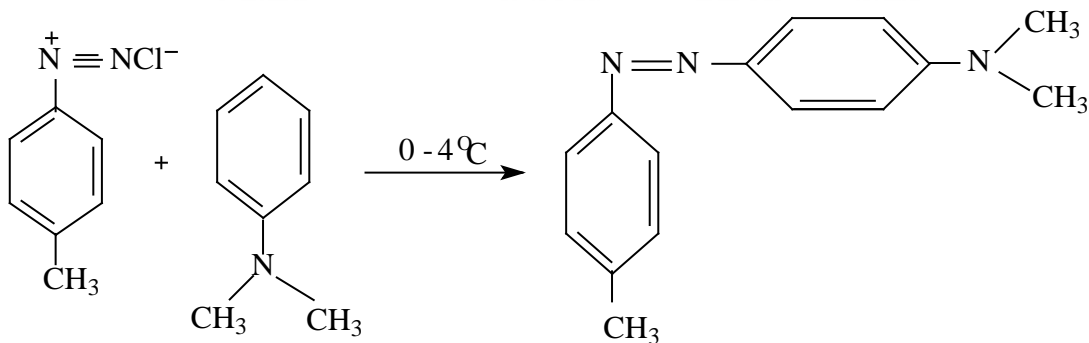


Scheme 1.

Coupling with N, N-dimethylaniline:

In a 250 cm³ beaker, N, N-dimethylaniline (5.2 g, 0.035 mole) was dissolved in 25 ml of acetic acid. The Solution was then cooled in an ice bath at 4°C.

The Diazonium salt of 4-methylaniline was added slowly into the Coupling Component while stirring. The precipitate obtained was then be filtered and washed with water till all the acid was washed away. It was then be dried room temperature.



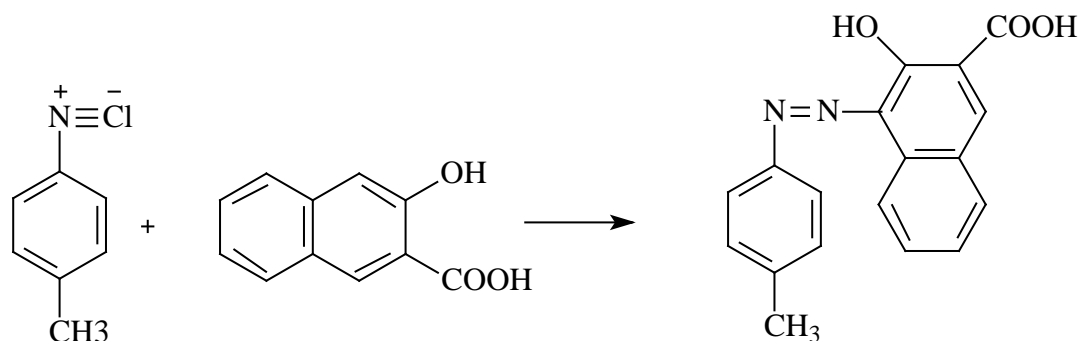
Coupling reaction with N,N- dimethylaniline

Scheme 2.

Coupling with Beta-Hydroxynaphthionic Acid (BON ACID):

In a 250 cm³ beaker, Bon acid (5.2 g, 0.035 mole) was dissolved in a solution of hydroxide pellet 7.0 g and water (25 cm³). The Solution was cooled in an Ice bath at 4°C. The Diazonium salt of 4-methylaniline was added slowly

while stirring the Solution. The Solution was filtered with a filter paper and then washed with water until all the Acid was washed away. It was then dried at room temperature



Diazonium salt of 4-methylaniline Bon Acid

Dye B **Scheme 3.**

Characterization of the Synthesized dyes

Determination of Percentage Yield.

The percentage yield of the synthesized dyes was determined using the formula Percentage Yield.

$$\% \text{ Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

Determination of Melting Point

The melting point of the dye was obtained by Using Gallankamp Melting Point apparatus. Small amount of the Sample was filled into a capillary tube and placed into the apparatus, the melting point of the Sample was then obtained by Consistently Focusing on the apparatus gradually heat the Sample and then values recorded.

UV- Visible Spectroscopy

The Agilent carry 300 UV-spectrophotometer was used. The cells used for the Spectrometric analysis was washed thoroughly with distilled water and air dried. Ethanol was then placed in the cell to take blank. It was then followed later by taking 5.0ml of the absorbance of the synthesized dyes (0.00005 mol/L) to reduce the concentration of the Sample. The Absorbance of the dye sample was then determined Spectrophotometer machine (UV-Visible Spectroscopy) within the visible region (i.e. 400-800 nm), In order to determine the wavelength of maximum absorption. The Procedure was repeated using DMSO.

Fourier Transform- Infrared Spectroscopy (FT-IR)

Aglet carry 630 FT-IR Spectrometer machine was used for the determination of IR spectrum of the synthesized dye sample in order to ascertain the functional group present in the dyes.

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 pellet 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:

$\sigma = l/RA$. Where σ is the electrical conductivity, l is the thickness of the dye pellet ($l = 2.45\text{mm}$), 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 $d = 3.89\text{cm}$ hence $r = 1.945\text{cm}$.Hence :

$$A = 3.142 \times (1.945 \times 10^{-2})^2$$

$$A = 1.1886 \times 10^{-3} \text{m}^2$$

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

Results and Discussion

Physical Properties of the Synthesized Dyes.

Table 1

Dye	Molecular formular	Molecular weight(g/mol)	Melting point °C	Percentage yield %	Color of dye
A	C ₁₅ H ₁₇ N ₃	239	130.5-137.9	86	Orange
B	C ₁₇ H ₁₆ O ₃ N ₂	296	179.5-231.8	80	Orange

Table 1: The Physical Properties Of the Synthesized dyes:

The melting point was determined using gallankamp melting point apparatus, in which dye A is having a melting point range of 130.5 °C to 137. 9 °C and dye B is having a melting point range of 179.5 °C to 231.8 °C. Dye B havening the highest melting point simply because of its molecular weight. The closeness in range of the melting point indicates the purity of the synthesized dye.

Table 2: Visible Absorption Spectra of Synthesized Dyes (λ_{max} in Ethanol and Dimethylsulfoxide (DMSO) Solvent (nm))

Dyes	Ethanol(nm)	DMSO(nm)
A	358.00	444.00
B	390.00	455.00

The result of wavelength of maximum absorption (λ_{max}) of the synthesized dyes in ethanol and dimethylsulfoxide (DMSO) solvent are shown below.

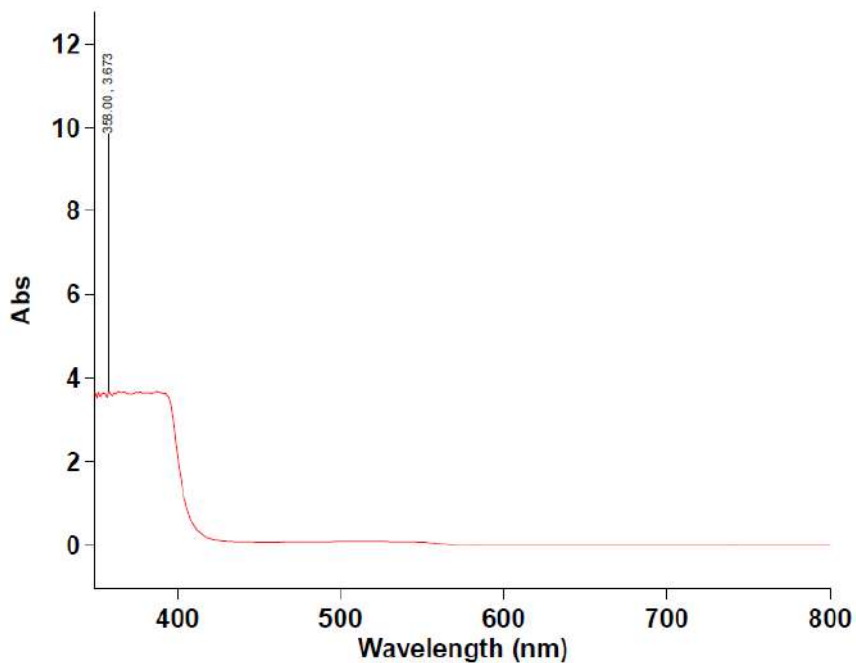


Fig. 1

Fig. 1: Visible absorption spectral of dye A in Ethanol

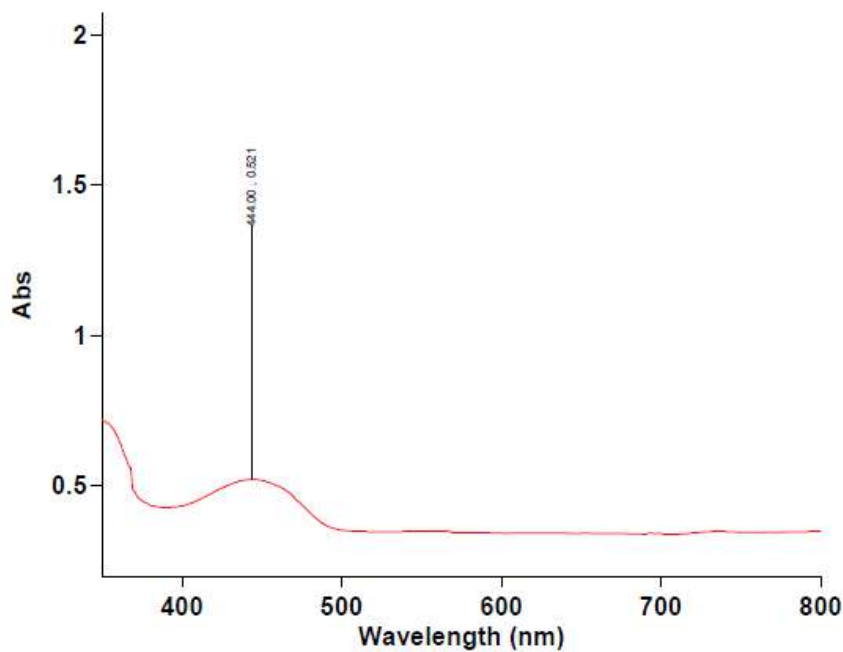


Fig.2

Fig. 2: Visible absorption spectral of dye A in DMSO

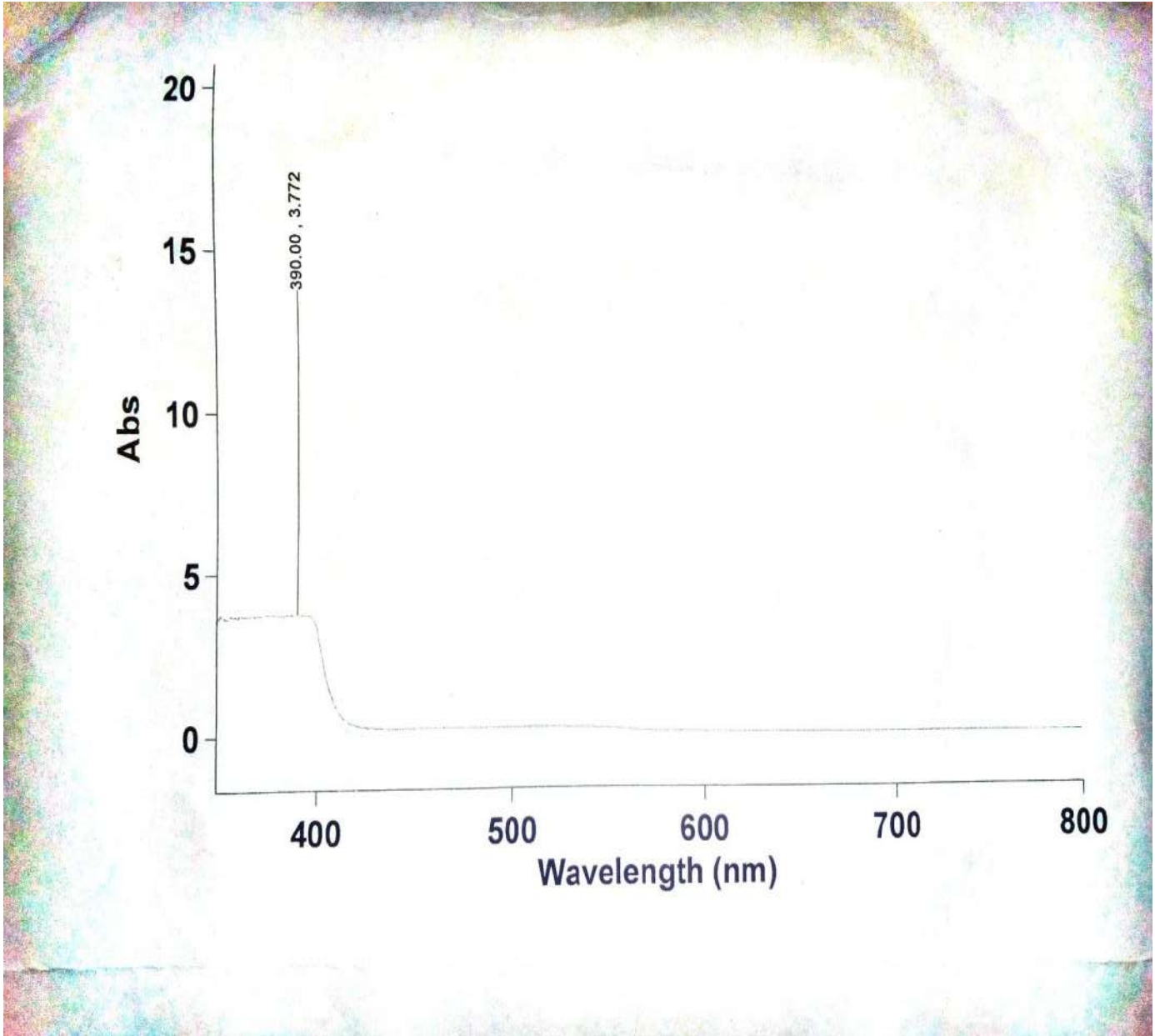


Fig. 3

Fig. 3: Visible absorption spectral of dye B in Ethanol

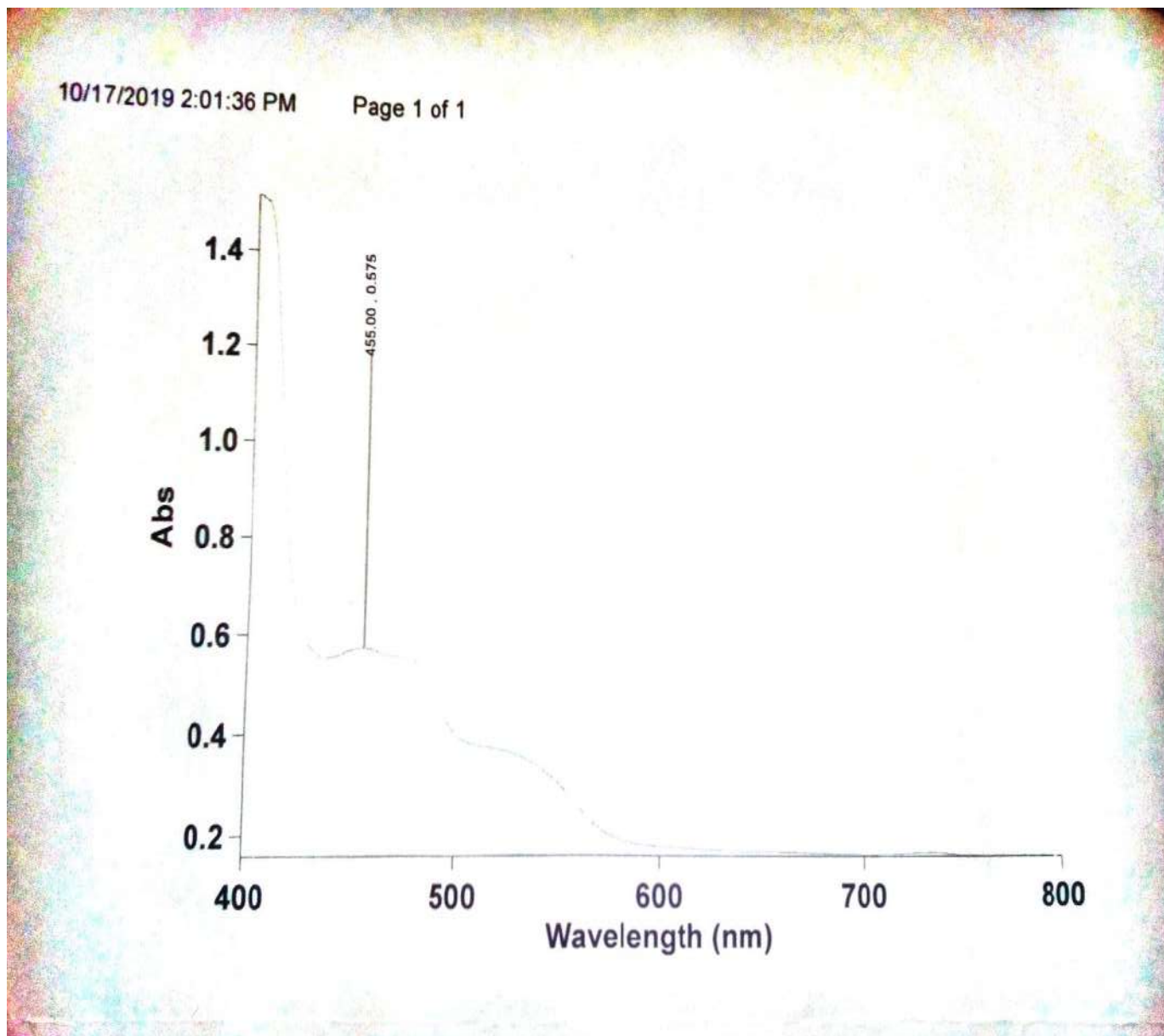


Fig.4

Fig. 4: Visible absorption spectral of dye B in DMSO

The result from Table 2 indicate the UV-visible spectra thus the maximum absorption for dye A is 358.00 nm and 444.00 nm for both ethanol and DMSO solvents respectively. Dye B happens to have the highest wavelength of maximum absorption of 390.00 nm and 455.00 nm for both ethanol and DMSO solvents respectively, because DMSO have higher polarity as compared to ethanol.

The Infra-red Absorption of the Synthesized Dyes

Table 3 IR-Vibrational Frequencies of the Synthesized Dyes IR V Max (cm⁻¹)

Dyes	IR V _{max} (cm ⁻¹)
A	3362.1(NH), 2914.8(CH-stretch), 1654.9, 1580.4, 1543.1 cm ⁻¹ (N=N)
B	3276.3cm ⁻¹ (OH-stretch), 2814.1(CH-stretch), 1654.9, 1625.1, 1513.3(N=N)

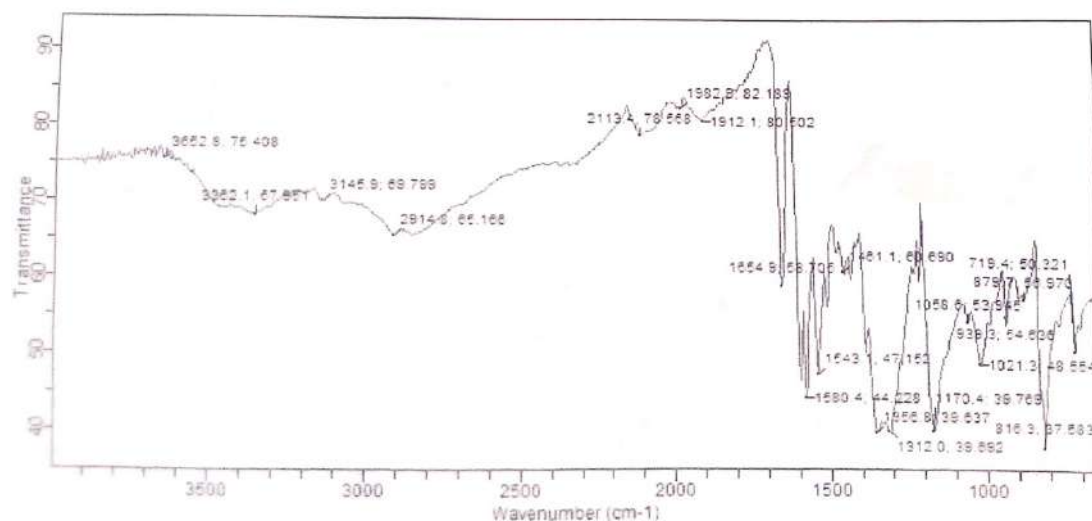
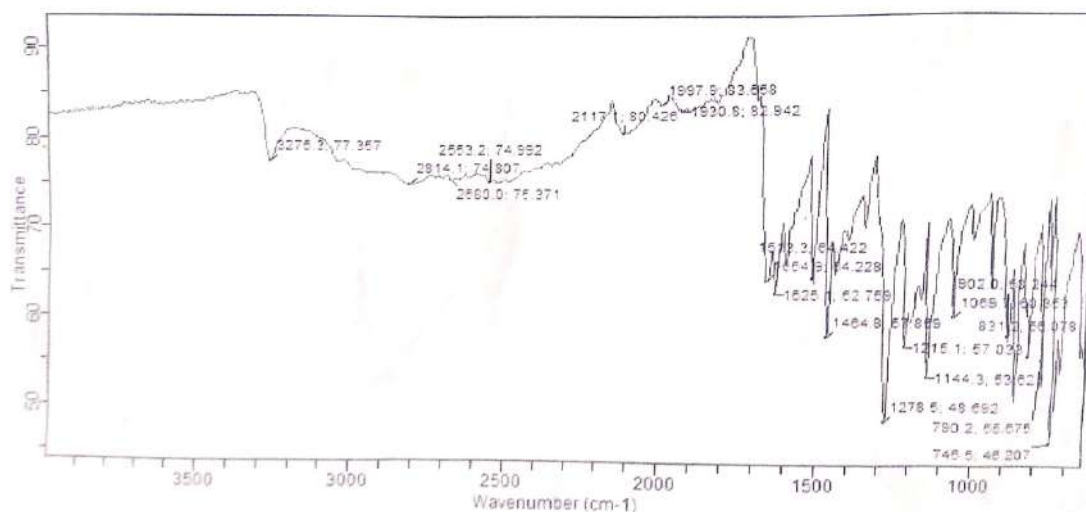


Fig. 4.5; FT-IR Spectra of Dye A////



Fourier Transform infra-red (FT-IR) spectra of the synthesized dyes:

The results shows the functional groups and the vibrational frequency present in the synthesized dye ; 3362.1 cm^{-1} NH Amine stretch , 2914.8 cm^{-1} CH- stretch, 1654.9 cm^{-1} , 15804 cm^{-1} , 1543.1 cm^{-1} N=N stretch, vibrations.

Then dye B is 3276.2 cm^{-1} , OH- stretch, 2814.1CH-strech, 1654.9, 1625.1, 1513.3 N=N stretching vibration respectively.

THE ELECTRICAL CONDUCTIVITY OF THE SYNTHESIZED DYES WITH CHANGE IN FREQUENCY AT 60 HZ

TABLE 4: ELECTRICAL CONDUCTIVITY OF SYNTHESIZED DYES AT 60 Hz

Sample	Electrical conductivity (S/m)
A	5.96E-09
B	2.61E-06

the result showed variation of electrical conductivity of the synthesized dyes with change in frequency and the result obtained shows that dye A and dye B have relatively stable electrical conductivity with the frequency change. The observed relative stability of the electrical conductivity of Dye B, over the frequency range may be ascribed to the fact that at low frequencies the materials may have had time for both fast dipole polarizations to occur as well as slower segmental polarization to occur, thus influencing the electrical behavior of the material. This may also be linked to the ability of the electrons within the molecules of the synthesized compound to respond to the applied current (Mohammed and Mustapha, 2010). Comparison of the electrical conductivity of the dyes at 60 Hz as shown in Table 4.0, the electrical conductivity of the synthesized dyes were observed to be within the range of 10^{-6} - 10^{-9} S m^{-1} . The electrical conductivity of the dyes lies within the range of electrical conductivity for semiconductor which is between 10^{-12} - 10^2 S m^{-1} (Aziz et al., 2002). However, Dye B was observed to have the highest electrical conductivity of 2.61×10^{-6} S m^{-1} at 60 Hz. This can be attributed to the fact that dye B have continuous conjugation due to the presence of betaoxynaphthionic acid and hence have higher electrical conductivity. Their higher electrical conductivity can also be attributed to the presence of electron withdrawing group of carboxylic acid. Thus, the electrical conductivity value of synthesized dyes was in agreement with literatures.

Conclusion

Different polyaniline substituted dyes were synthesized by the substitution of the dyes moieties on the polyaniline backbones. Their physicochemical properties were assessed and spectroscopic analysis such as Fourier Transform Infra Red Spectrometry, and GC-MS were used to elucidate the structures. The electrical conductivity was carried out using programmable LCR meter at a frequency range of 200-100000 Hz and the result shows that the electrical conductivity of synthesized polyaniline substituted dyes lies within the range of 10^{-2} - 10^{-4} S. m^{-1} . Therefore the electrical conductivity of the synthesized polyaniline substituted dyes were observed to lies within the range of electrical conductivity for semiconductor of 10^{-12} – 10^2 S.m^{-1} .

CONCLUSION

Azo dyes were synthesized using 4-methylaniline as the diazo component, Beta-hydroxynaphthionic Acid (BONACID) and N, N-dimethylaniline as the coupling component, where the wavelength of maximum absorption were at 358.00 nm on the solvent Ethanol and 444.00 nm on the solvent DMSO for dye A and 390.00 nm on the solvent Ethanol and 455.00 nm on the solvent DMSO for dye B. FT-IR spectroscopy gives the functional group present in each of the dye. The electrical conductivity of the synthesized dyes were observed to be within the range of 10^{-6} - 10^{-9} S m⁻¹. The electrical conductivity of the dyes lies within the range of electrical conductivity for semiconductor which is between 10^{-12} - 10^2 S m⁻¹. However, Dye B was observed to have the highest electrical conductivity of 2.61×10^{-6} S m⁻¹ at 60 Hz.

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