



## SYNTHESIS AND CHARACTERIZATION OF AN AZO DYE AND ITS IRON COMPLEX

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### ABSTRACT

An azo dye and its iron complex have been synthesized and characterized using IR and UV-Vis spectrophotometer. The azo dye was prepared by coupling 3-aminophenol and 2-naphthol after which the iron complex was synthesized by coupling the unmetallised dye with  $\text{FeCl}_3$ . The unmetallized dye has its maximum absorption wavelength at 436.00 nm while the metal complex dye has 341.50 nm. The IR spectra showed the value of  $\text{N}=\text{N}$ - stretching frequency at  $1458.23\text{cm}^{-1}$  for both the unmetallised dye and its metal complex, and which is within the range of  $1400\text{-}1500\text{ cm}^{-1}$ . This indicates that the synthesized complexes contain azo an azo group. The IR spectra showed the value of  $\text{C}-\text{N}$  frequency at  $1267.27\text{ cm}^{-1}$  for both the unmetallised dye and its metal complex. Also, The IR spectra showed the value of  $\text{O}-\text{H}$  frequency at  $3408.33\text{cm}^{-1}$  for dye while  $3402.54\text{ cm}^{-1}$  for metal complex dye.  $\text{C}=\text{C}$  has the IR spectra frequency of the dye at  $1514.17\text{ cm}^{-1}$  which is within the range of  $1450\text{-}1600\text{ cm}^{-1}$ . The metal complex dye shows the IR value of  $\text{Fe}-\text{N}$  at  $263\text{ cm}^{-1}$  and  $\text{Fe}-\text{O}$  at  $576\text{ cm}^{-1}$ .

**Keywords:** 3-aminophenol, 2-naphthol, Unmetallized dye, Complex, UV-Vis.

### INTRODUCTION

Dyes play an indispensable role in human history since ancient times. Dyeing processes are often considered an important characteristic of a particular civilization or culture. Dyes are used in almost every commercial product such as food, clothing, pigments and paints (Puntener, 2012). The Azo group is characterized by a lone pair of orbitals containing two electrons on the nitrogen atom, if linked to an aromatic ring carrying additional donor sites is well suitable for chelation. The majority of these compounds are derived from the coupling of diazotized heterocyclic amines with aromatic hydroxyl and amino compounds. This type of molecule has several advantages. To quote a few, the azo group is photochromic, redox responsive, pH-sensitive, stabilizes low valence metal oxidation states due to the presence of a low-lying azo centered  $\pi^*$  molecular orbital, is used as a metal ion indicator in complexometric titration, dyes and pigments in the textile industry (Emel and Boztepe, 2002). Azo dyes have a general structure  $\text{R}-\text{N}=\text{N}-\text{R}'$ , where R and R' are aryl, alkyl, or heterocyclic groups. Monoazo dyes have only one  $\text{N}=\text{N}$  double bond, while diazo and triazo dyes contain two and three  $\text{N}=\text{N}$  double bonds, respectively (Hoffmann and Puszynski, 2020). The azo groups are generally connected to benzene and naphthalene rings. They are usually prepared through the condensation of azo compounds with ketones or aldehydes. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy- groups are commonly used coupling components (Braz, 2016).

The syntheses involve Low-cost, readily available commodity organic starting materials such as aromatic amines and phenols. The solvent in which the reactions are carried out in water, which offers obvious economic and environmental advantages over all other solvents. It is likely that in the future, azo dyes are likely to assume even greater importance as some of the other chemical types, notable anthraquinones, become progressively less economic. In terms of their colour properties, azo dyes are capable of providing virtually a complete range of hues. There is no doubt though that they are significantly more important commercially in yellow-brown, orange and reddish-brown colours (*i.e.* absorbing at shorter wavelengths), than in blues and greens. Azo dyes are capable of providing the high intensity of colour, about twice that of the anthraquinones, and reasonably bright colours (Prival, 1998). They are capable of providing reasonable to very good technical properties, for example, fastness to light, heat, water and other solvents, although in this respect they are often inferior to other chemical classes, for example, arboyl and phthalocyanine dyes, especially in terms of light fastness. The prime reason for the commercial importance of azo dyes is that they are the most cost-effective of all the chemical classes of organic dyes and pigments (Abd-Alredha, 2012).

### MATERIALS AND METHODS

#### Materials and Reagents

The materials used for this work are; Erlenmeyer flask (250 ml), Filter papers, Spatula, Beakers of various sizes, Heater,

Analytical weighing balance (Digital), Measuring cylinder (10 ml) Water bottle, Thermometer ( $^{\circ}\text{C}$ ), Stirrer, Ice bath, Sample bottles. The Reagents are; 3-aminophenol, 2-naphthol, Concentrated HCl, 1M and 0.1M NaOH, Sodium Nitrite ( $\text{NaNO}_2$ ),  $\text{FeCl}_3$ , Methanol, Acetone, Chloroform, Ethanol and Distilled Water.

### Production of a dye by coupling 3-aminophenol with 2-naphthol

The dye was prepared with slight modification of the method of David (2008) as follows:

2.00 g of 3-aminophenol was weighed and dissolved in a conical flask (A) containing 30 ml of distilled water. 5 ml of Conc. HCl was slowly added and stirred until complete dissolution. The solution was cooled in an ice-water bath until its temperature is below  $5^{\circ}\text{C}$ . 2.00 g of 2-naphthol was dissolved in 10 ml of 1M

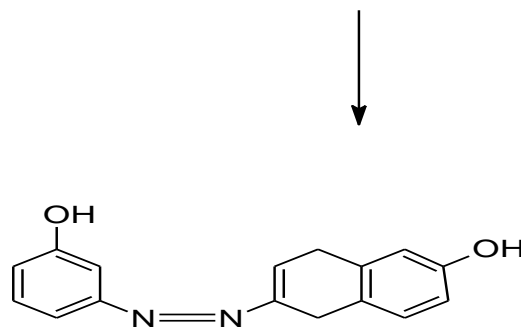
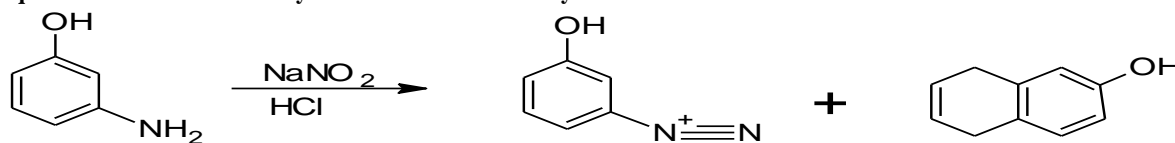
NaOH in an Erlenmeyer flask (B). 0.35 g of  $\text{NaNO}_2$  was added into a 5 ml of distilled water in a test tube (C). The solution prepared in (C) was transferred into the solution prepared in (B). 10 g of crushed ice was placed in a 500 ml beaker (D) and 3ml of conc. HCl was added. The solution prepared in (B) was transferred into (D) and stirred for 7 minute to form the diazonium salt. The solution was then cooled below  $5^{\circ}\text{C}$ . The solution in (A) was transferred into (D) and stirred. The solution was kept for 24 hours before it was filtered, wash and dried.

**Preparation of metal complex dye** 0.6 g of unmetallised dye was dissolved in 10 ml of methanol in a beaker. The solution was heated to  $80^{\circ}\text{C}$  while stirring. A 0.6 g of  $\text{FeCl}_3$  was added in a 10 ml beaker to the mixture. 3 ml of 0.1 M NaOH was added to adjust the pH to 8. The mixture was stirred at  $80^{\circ}\text{C}$  for 25 minutes. The product was filtered, wash with methanol and air-dried.

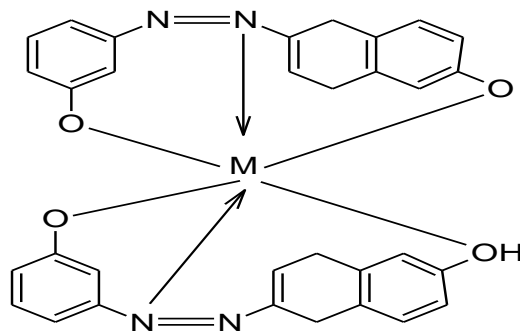
## RESULTS AND DISCUSSIONS

### Result

#### Equation of reaction for the synthesis of unmetallised dye



6-[(Z)-(3-hydroxyphenyl)diazenyl]-5,8-dihydronaphthalen-2-ol



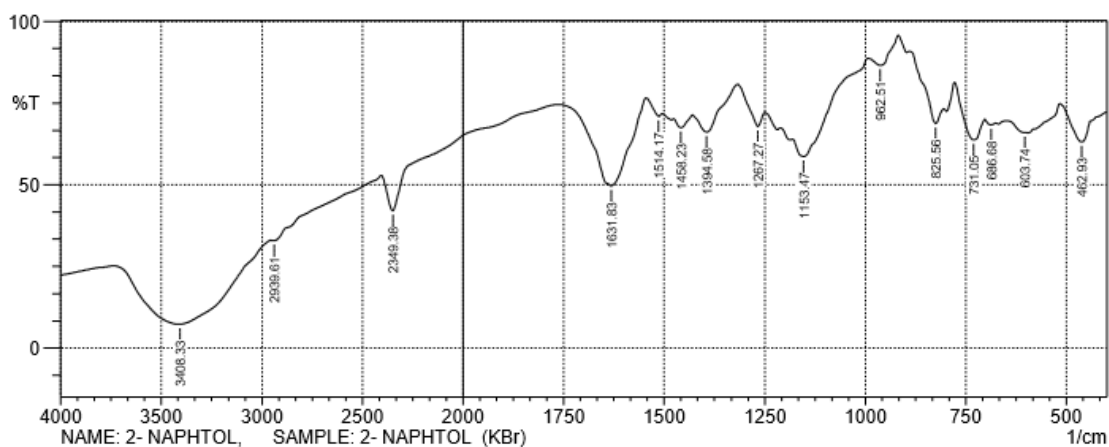
Proposed metal complex dye where  $\text{M} = \text{Fe}$

**Table 1: Names and Properties of dyes**

DYE	NAME OF DYE	COLOUR	TEXTURE	MOLECULAR MASS (g/mol)	PERCENTAGE YIELD
DYE 1	6-[(z)-(3-hydroxyphenyl)diazenyl]-5,8-dihydronaphthalen-2-ol	Deep brown	Powdery solid	253.30	85%
DYE 2	1:2 Iron metal complex	Reddish Brown	Powdery solid	309.15	50%

**Table 2: Absorption spectra table**

PARAMETERS	DYE	METAL COMPLEX
$\lambda_{\text{max}}$ (nm)	436.00	341.50
Absorbance	0.287	5.000

**Figure 1: FTIR result of unmetallized dye****Table 3: FTIR Result of Unmetallised dye**

FUNCTIONAL GROUP	EXPERIMENTAL PEAK (cm <sup>-1</sup> )	LITERATURE	REFERENCES
N=N	1458.23	1400-1500 cm <sup>-1</sup>	<a href="http://www.faculty.mu.edu.sa">www.faculty.mu.edu.sa</a>
O-H	3408.33	3100-3600 cm <sup>-1</sup>	www. Orgchem.colorado.edu
C-N	1267.27	1000-1350 cm <sup>-1</sup>	www. Orgchem.colorado.edu
C=C	1514.17	1450-1600cm <sup>-1</sup>	www. Orgchem.colorado.edu

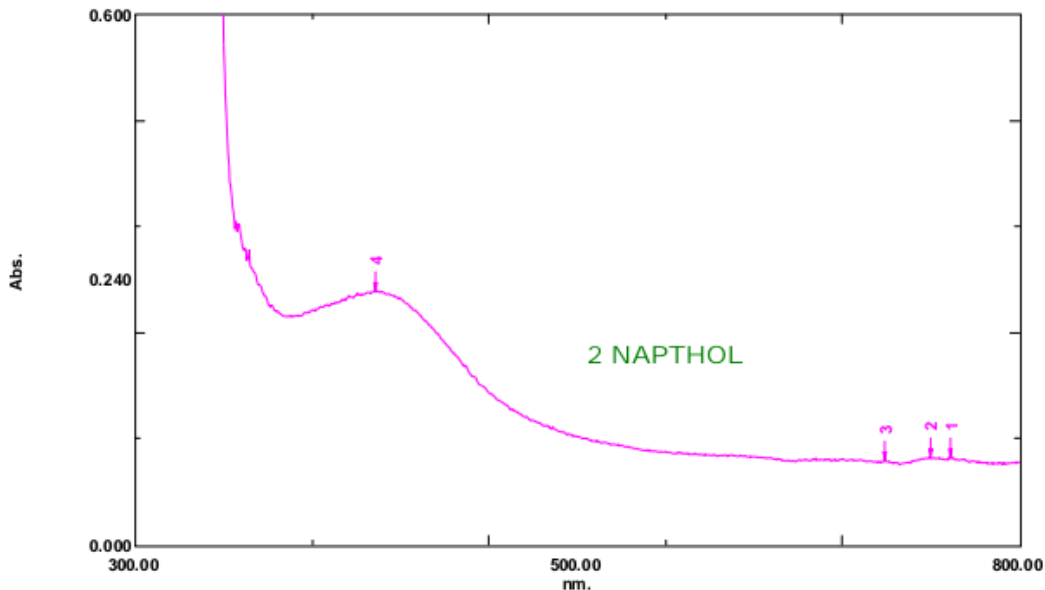


Fig. 2: UV-VIS spectra result of unmetallised dye

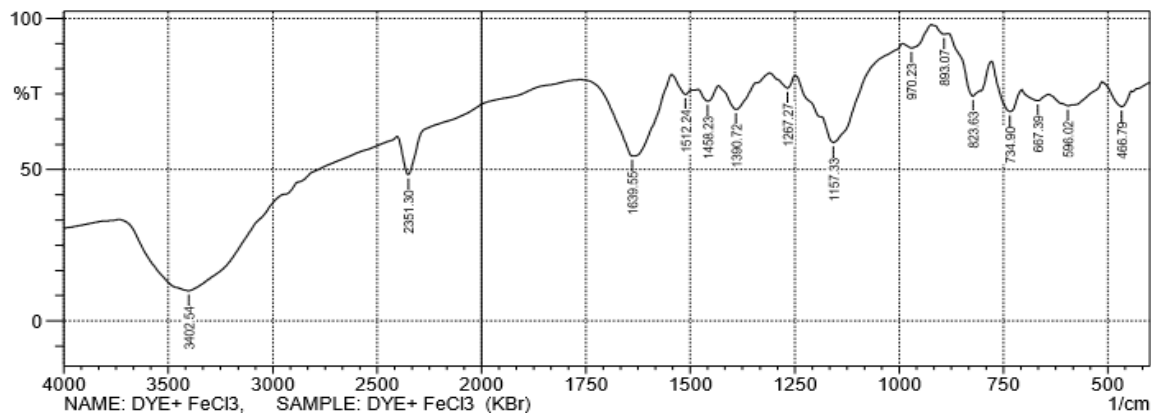


Figure 3: FTIR Result of metal complex dye

Table 4: FTIR result of metal complex dye

FUNCTIONAL GROUP	EXPERIMENTAL PEAK (cm <sup>-1</sup> )	LITERATURE	REFERENCES
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N=N	1458.23	1400-1500 cm <sup>-1</sup>	<a href="http://www.faculty.mu.edu.sa">www.faculty.mu.edu.sa</a>
O-H	3402.23	3100-3600 cm <sup>-1</sup>	www. Orgchem.colorado.edu
C-N	1267.27	1000-1350 cm <sup>-1</sup>	www. Orgchem.colorado.edu
Fe-N	854	700-1000 cm <sup>-1</sup>	Saratovskikh, 2013
Fe-O	576	500-4000 cm <sup>-1</sup>	Braz, 2016

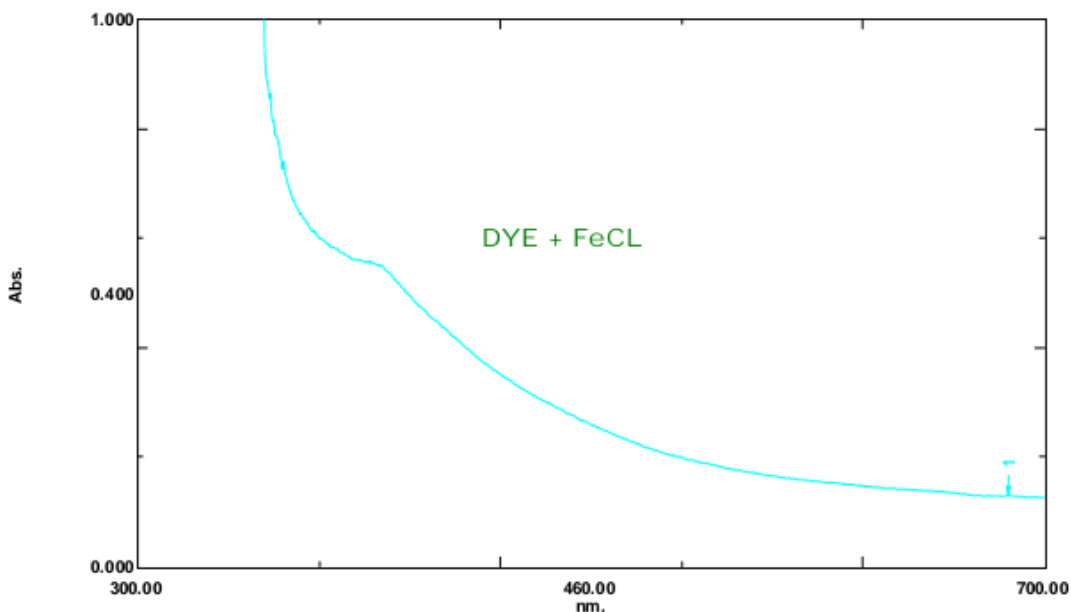


Figure 4: UV-VIS Result of metal complex dye

Table 5: Solubility Test of Unmetallized Dye and Metal Complex

SOLVENTS	UNMETALLIZED DYE	METAL COMPLEX
Ethanol	SS	SS
Chloroform	IS	S
Methanol	S	SS
Acetone	S	S
Water	IS	IS

Where S=Soluble, SS=Slightly Soluble, IS=Insoluble

## DISCUSSION

The metal complex dye was synthesized by reacting 3-aminophenol and sodium nitrite to form a diazonium salt which was then coupled with 2-naphthol to give an unmetallized dye. The unmetallized dye was reacted with  $\text{FeCl}_3$  to give a metal complex.

The absorption maximum of the unmetallized dye was 436.00 nm and that of the metal complex dye was 341.50 nm. The change in the absorption maximum of the metal complex from its ligand indicates the coordination of the ligand to the metal. This agrees with the findings of Abd-Alredha *et al.* (2012).

The IR spectra showed the value of  $-\text{N}=\text{N}-$  stretching frequency at  $1458.23 \text{ cm}^{-1}$  for both the unmetallized dye and its metal complex, and which is within the range of  $1400-1500 \text{ cm}^{-1}$ . This

indicates that the synthesized complexes contain azo group. The IR spectra showed the value of C-N frequency at  $1267.27 \text{ cm}^{-1}$  for both the unmetallized dye and its metal complex. Also, the IR spectra showed the value of O-H frequency at  $3408.33 \text{ cm}^{-1}$  for dye while  $3402.54 \text{ cm}^{-1}$  for metal complex dye. C=C has the IR spectra frequency of the dye at  $1514.17 \text{ cm}^{-1}$  which is within the range of  $1450-1600 \text{ cm}^{-1}$ . The metal complex dye shows the IR value of Fe-N at  $263 \text{ cm}^{-1}$  and Fe-O at  $576 \text{ cm}^{-1}$ .

The percentage yield obtained for the dye is 85% while the metal complex dye has 50%. The metal complex has a low yield due to interference caused by instrumental error which contains some impurities and tends to react with the work.

The molecular masses obtained for the complexes are  $253.30 \text{ g/mol}$  for 6-[(z)-(3-hydroxyphenyl)diazenyl]-5,8-

dihydronaphthalen-2-ol and 309.02 g/mol for 1:2 iron metal complex respectively.

### CONCLUSION

An azo dye (3-aminophenol and 2-naphthol) and its metal complex (1:2 iron metal complex) were synthesized and characterized by FTIR and UV-Vis spectrophotometer. The proposed structure of the dye and its metal complex has been established. The unmetallised dye has a maximum absorption wavelength of 36.00 nm while the metal complex has 341.50 nm. The vibrating frequencies of the unmetallised dye and its complex fall within the range of IR spectra as provided by reviewed pieces of literature. The physical properties of the dye and complex synthesized were also determined.

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