



## SYNTHESIS AND DYEING PERFORMANCE OF HETEROCYCLIC DYES CONTAINING AMINOTHIOPHENE MOIETY ON POLYESTER FIBRE

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### ABSTRACT

*New Azo dyes derived from aminothiophene as a diazo component with Gamma acid, Tobais acid, and J-acid as coupling components were successfully synthesised. The identity of the dyes was assessed using spectroscopic analysis such as UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy and melting point. The melting point of the intermediate was observed to be 200-208 °C, while that of the dyes ranges from 195-210 °C. The percentage yield of the intermediate was calculated to be 48%, while that of the dyes ranges from 55-60%. The dyes absorbed within the visible region of the electromagnetic spectrum in ethanol as solvent ranging from 568-589 nm. The infra-red spectra of the dyes confirmed the presence of the functional groups such as NH/OH at the vibrational frequency range of 3402.50-3410.26 cm<sup>-1</sup>, aromatic Hydrogen group (Ar-H) at 2924.18 cm<sup>-1</sup>, C=O group at the frequency of 2322.37 cm<sup>-1</sup>, CN stretch at 1643.41 cm<sup>-1</sup>, Azo chromophoric group (-N=N) appear at the frequency range of 1411.94-1527.67 cm<sup>-1</sup> and S=O functional group at the vibrational frequency range of 1149.61-1157.33 cm<sup>-1</sup> respectively. The dyes gave different shades on polyester fabrics and exhibited very good to excellent fastness properties to washing and light.*

### KEYWORDS

Aminothiophene, polyester fibre, diazotization, coupling reaction, heterocyclic dyes

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### INTRODUCTION

Azo dyes used to be among the leading colouring agents in the textile industry, especially in developing countries. Azo dyes produce bright, high-intensity colours, have fair to good fastness properties, are economical to produce and account for more than half of all commercial dyes used

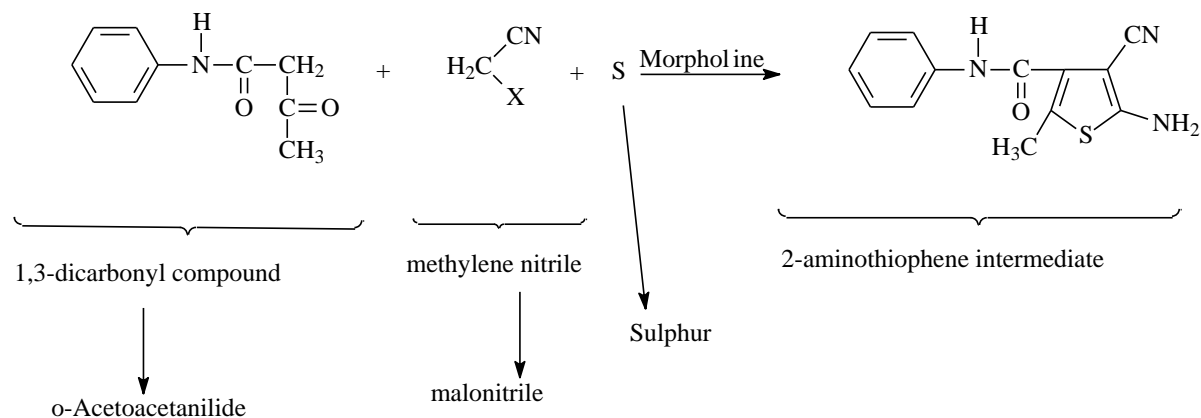
(Zollinger, 2017). Generally, they are characterised to have at least one azo linkage (-N=N-) attached to the aromatic ring at one end and carbocyclic, heterocyclic or aliphatic type of unsaturated molecules at the other end (Venkataraman, 2012). The synthesis and application of heterocyclic dyes have further opened up ways for dyestuff research to graduate from purely empirical synthesis of coloured molecules to the study of the mechanism of interaction of substrate and dyes with which already known chromogens such as azo, anthraquinone and cyclic azo compounds are associated.

Different dyes are now synthesised worldwide with these improvements and synthesis knowledge (Ahmed, 2014). Aminothiophenes are important five-membered heterocyclic building blocks in organic synthesis, and the chemistry of these small molecules is still developing based on the discovery of cyclisation by Gewald. Another attractive feature of aminothiophene scaffolds is their ability to act as synthons for synthesising biologically active thiophene-containing heterocycles, conjugates and hybrids (Abrahart, 2012). The application of 2-aminothiophenes or their 2-N-substituted analogues in textile dyeing is still being investigated because of their various mechanisms of action (Aliyu, 2017).

## **EXPERIMENTAL**

### **Synthesis of Aminothiophene Intermediate**

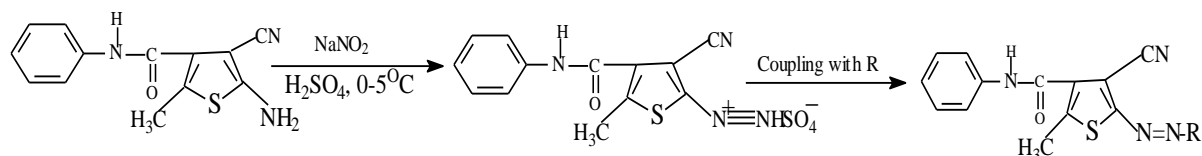
The aminothiophene intermediate was synthesised following Gewald's methods reported by Alaa and Tarek (2006). O-acetoacetanilide (21.16 g, 0.1 mol), malononitrile (6.96g, 0.1mol) and sulphur (3.37 g, 0.1 mol) in 30 ml ethanol were stirred in the presence of morpholine (8.97g, 0.1mol) at 60-70 °C for 3 hours. The resulting thick dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with ethanol, and then ethanol/water (1:1) solution and drying. The brown powder was then recrystallised from ethanol.



### Diazotisation of 2-Aminothiophene Intermediate and Coupling Reaction

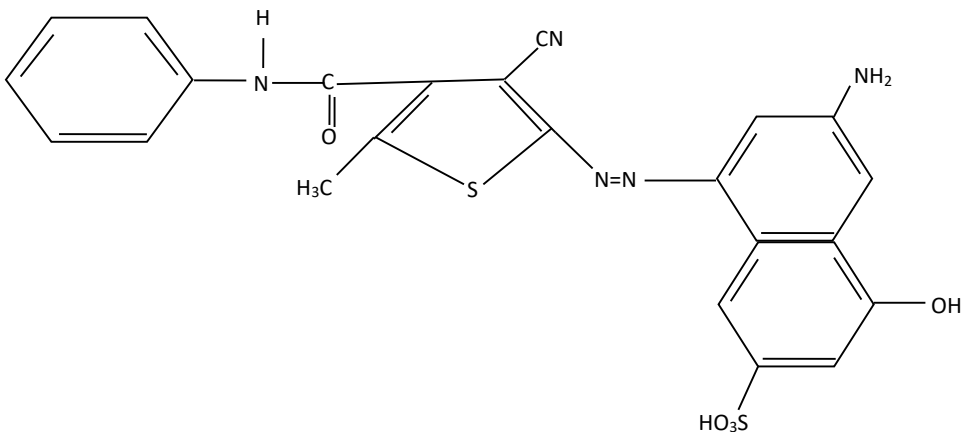
Sodium nitrite (1.38g, 0.02mol) was added dropwise to 10 ml of concentrated sulphuric acid at 10 °C and heated to 60°C with stirring for 15 minutes. The solution was cooled to 5 °C and a mixture of acetic acid and propionic acid (17:3) was added to the mixture below 30 °C. The finely ground aminothiophene intermediate (4.90g, 0.02 mol) was slowly added within 30 minutes below 5 °C and the whole mixture was stirred at 0-5 °C for 2 hours.

The excess nitrous acid (tested for using starch iodide paper) was decomposed with the required volume of urea. The clear diazonium salt solution thus obtained was used immediately in the coupling reaction. The associated steps are illustrated in the reaction scheme below.

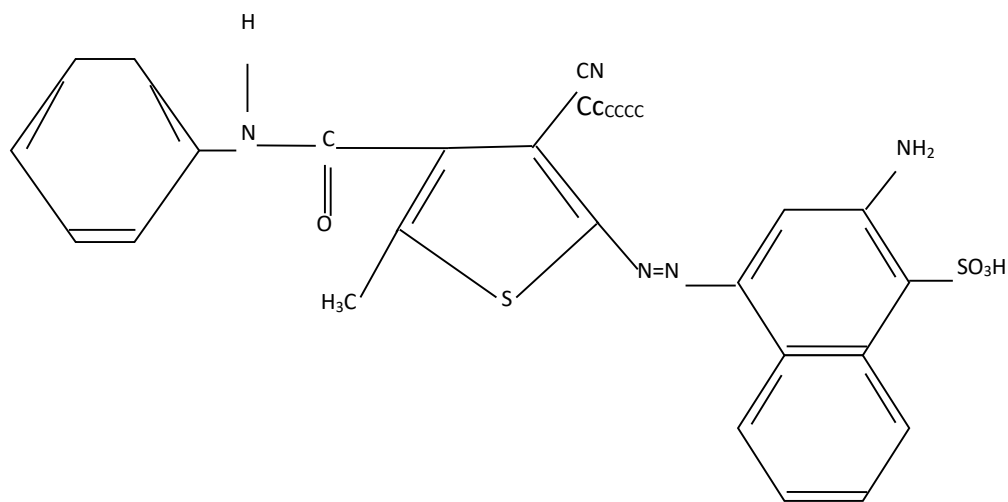


Where R represents coupling components (Gamma acid, Tobias acid and J-acid)

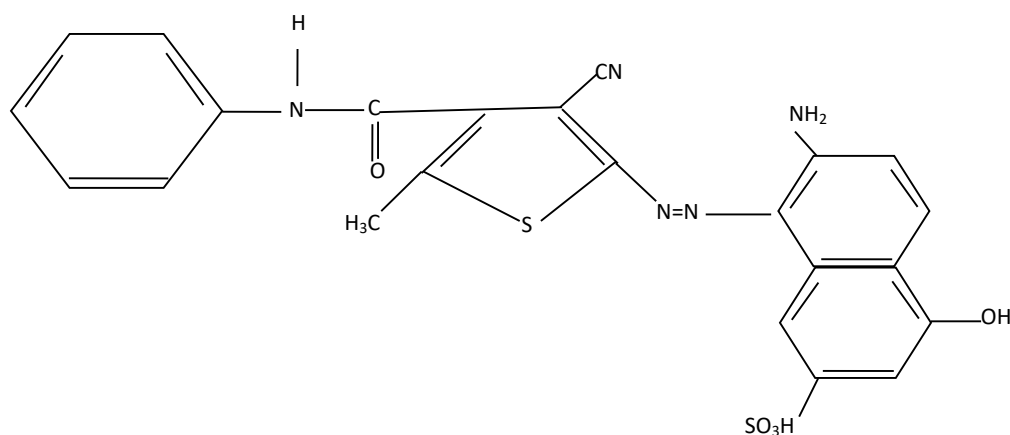
The proposed structures of the synthesised dyes are as follows



Dye 1: (Dye obtained from Gamma Acid as coupling component)



Dye 2: (Dye obtained from Tobias acid as coupling component)



Dye 3: (Dye obtained from J- acid as coupling component)

### Characterisation of the Synthesised Dyes and Intermediate

FT-IR spectra of the intermediate and the synthesised dyes were recorded on an Agilent CARY 630 FT-IR spectrophotometer, the visible absorption spectra of the dyes were recorded on an Agilent CARY 300 UV-visible spectrophotometer and the melting points of the dyes and 2-aminothiophene intermediate were determined by using Gallenkamp melting point apparatus.

### Application of Dyes

1 % stock solution of each Dye was prepared, a liquor ratio of 50:1 was used, 2 % shade on fabric weight (o.w.f.), and 1 g of polyester. The volume required from each stock solution was calculated based on the formula;

$$V = \frac{P \times W}{C}$$

where:

P = percentage shade

W = weight of fabric

C = percentage concentration of the stock solution.

The polyester fibre was introduced into the bath, and 5ml of formic acid was added. After that, it was run for 1 hour at 100 °C in a mechanical shaker at a controlled speed (Traubel & Eitel, 1977). The dyed fibre was removed from the dye bath, rinsed with running water and air-dried.

### Assessment of Fastness Properties

- The wash Fastness Test of the dyed polyester fibre was carried out by subjecting it to the I.S.O.3 wash fastness test method.
- The light Fastness Test of the dyed sample was carried out by subjecting it to the 8-Blue Wool Standard method.

## RESULTS

**Table 1:** Physical properties of intermediate and synthesized dyes

S/N	Sample	Melting Point (°C)	% Yield	Appearance
1	Intermediate	200-208	48	Brown
2	Dye 1	202-205	57	Deep Grey
3	Dye 2	195-200	55	Deep Pitch
4	Dye 3	204-210	60	Deep blue

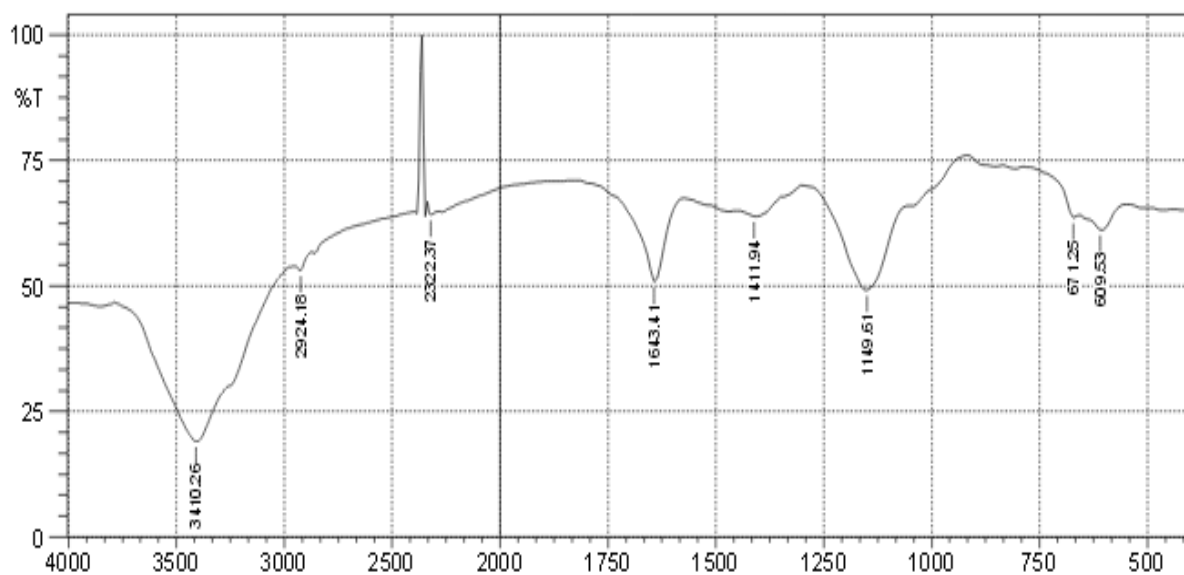
**Where:** Dye 1 is Dye from Gamma acid; Dye 2 is Dye from Tobias acid; and Dye 3 is Dye from J-acid.

**Table 2:** Visible absorption spectroscopy of dye

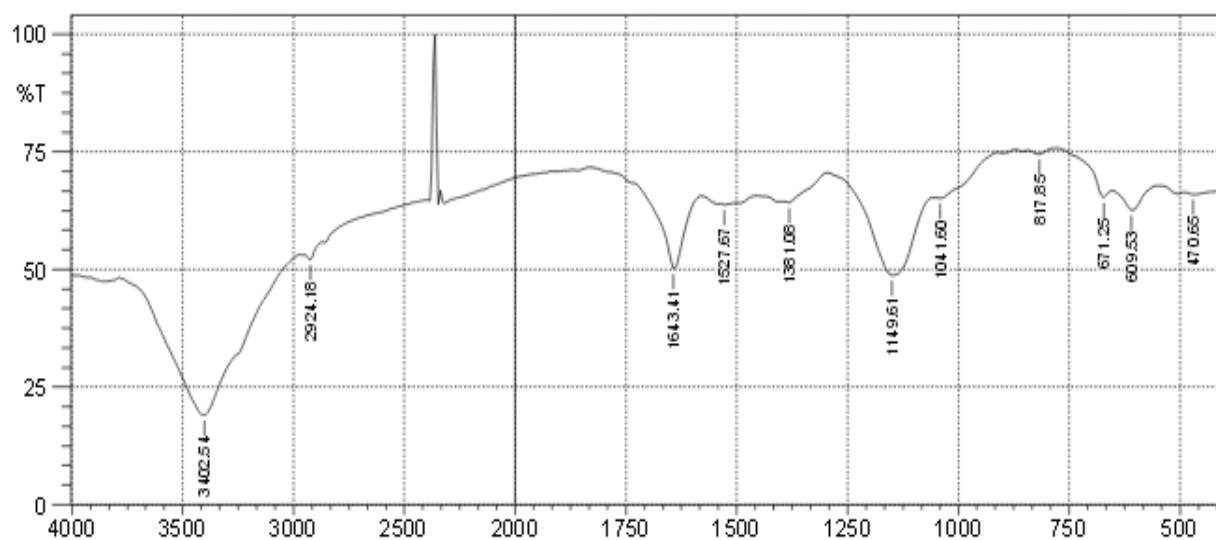
Sample	Ethanol ( $\lambda_{max}$ )
Dye 1	589.00
Dye 2	581.50
Dye 3	568.00

**Table 3:** Infra-red spectra of the dye

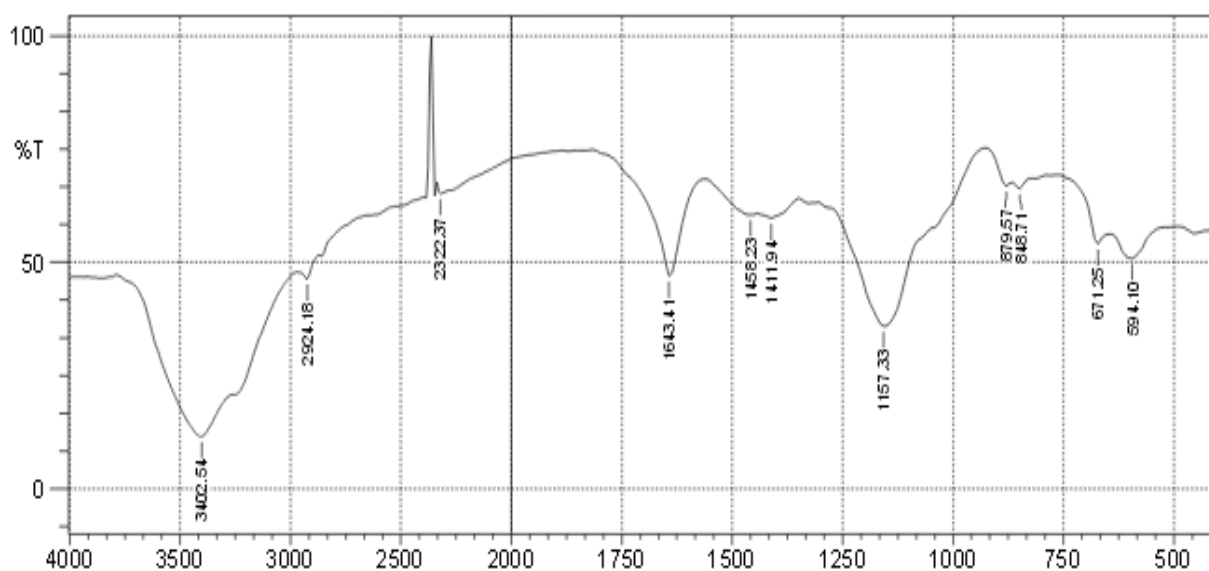
Sample	Vibration Frequencies (cm <sup>-1</sup> )
Dye 1	3410.26 (N-H/O-H stretch), 2924.18 (Ar-H stretch), 2322.37 (C=O stretch), 1643.41 (C=N stretch) 1411.94 (N=N Stretch), 1149.61 (S=O Bending Vibration)
Dye 2	3402.54 (N-H stretch), 2924.18 (Ar-H stretch), 1643.41 (CN stretch), 1527.67 (N=N Stretch), 1149.61 (S=O Bending Vibration)
Dye 3	3402.54 (N-H/OH stretch), 2924.18 (Ar-H stretch), 2322.37 (C=O stretch), 1643.41 (C=N stretch) 1458.23, 1411.94 (N=N Stretch) 1157.33 (S=O Bending Vibration)



FT-IR Spectra of Dye 1



FT-IR Spectra of Dye 2



FT-IR Spectra of Dye 3



**Table 4:** Wash fastness test using ISO 3 standard

Sample	Change in Color of polyester	Staining of Adjacent fabric	Colour on polyester
Dye 1	5	4/5	Grey
Dye 2	4	3/4	Pitch
Dye 3	5	5	Blue
Grey Scale (Change in shade/staining)			
5	Excellent	5	No staining
4	Very good	4	Very slight staining
3	Good	3	Moderate staining
2	Fair	2	Significant staining
1	Poor	1	Deep staining

**Table 5:** Light fastness test using 8-blue wool standards

Sample	Dyed Polyester fibre		
Dye 1	5		
Dye 2	5		
Dye 3	7		
Grey Scale (Change in shade/staining)			
Fastness grade	Degree of fading	Fastness grade	Degree of fading
8	None	4	Appreciable
7	Very slight	3	Significant
6	Slight	2	Extensive
5	Moderate	1	Very extensive

## DISCUSSION

### Physical Properties of the Intermediate and Synthesized Dyes

The melting point, percentage yield, and the appearance of the synthesised dyes are presented in Table 1. The colour of the dyes ranges from deep grey to deep blue appearance. All the dyes exhibited a well-defined melting point ranging from 195-210 °C with a percentage yield of 55-60%.

## **Visible Absorption Spectroscopy of Dye**

Table 2 contains the  $\lambda_{\text{max}}$  (wavelength of maximum absorption) of the dyes obtained in ethanol as solvent. All the dyes exhibited strong and broad Absorption in the visible region in ethanol at 568 to 589nm. The observed longer wavelength indicates the presence of colour-imparting chromophores responsible for the hues (Yu & Wei, 2006).

## **Infra-Red Spectra of Synthesized Dyes**

As observed from the IR spectra of the synthesised dyes in Table 3, all the dyes gave absorption peaks due to azo group N=N stretching vibration at the range of 1411.94-1527.67  $\text{cm}^{-1}$  and Absorption peaks of NH/OH stretching vibration at the range of 3402.54-3410.26  $\text{cm}^{-1}$  were also observed among the dyes.

The CN stretching vibration was observed at the frequency range of 1643.41  $\text{cm}^{-1}$ , C=O was confirmed at the vibration frequency range of 2322.37  $\text{cm}^{-1}$ , and S=O bending vibration was observed at the frequency range of 1149.61-1157.33  $\text{cm}^{-1}$ . In contrast, an absorption peak in the region 2924.18 $\text{cm}^{-1}$  due to Ar-H stretching vibration was observed for all the dyes.

## **Wash Fastness of the Synthesised Dyes on Polyester Using ISO 3 Standards.**

The wash fastness of the dyed polyester is presented in Table 4, and the result comprises the change in colour on the polyester and staining of the adjacent fabric. The colour of the dyes on the dyed substrate ranges from deep grey to deep blue shade with high tenorial strength and excellent levelness on the polyester.

The variation in the shade of the dyed polyester may result from the alteration in the coupling components. Thus, Dye 1 and 3 exhibited excellent fastness properties (grey scale 5) to washing, while Dye 2 exhibited very good fastness (grey scale 4). After washing, the remarkable degree of levelness and brightness indicates good penetration and excellent affinity of the dyes to the polyester fibre.

## **Light Fastness of the Dyes on Polyester Using 8 Using Wool Standards.**

The lightfastness rating of the dyed polyester fabric, as presented in Table 5, indicates moderate (5) to very slight (7) fastness. Light fastness is a property of a colourant such as Dye or pigment  
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that describes how resistant it is to fade when exposed to light; the bleaching of the colour is caused by the impact of ultraviolet radiation in the chemical structure of the molecule, giving the colour of the subject, the part of the molecules responsible for the colour is called a chromophore.

Light encountering a painted surface can either alter or break the chemical bonds of the pigment, causing the colours to bleach or change in a process known as photodegradation materials. This resistance to the effect is said to be the light fast. The rating obtained for a given colourant for any fading test depends on many factors, including concentration and degree of dye aggregation within the fabric. However, the lightfastness observed for the dyes ranges from 5-7, which could be ascribed to the coupling component used, the molecular structure of the dyes, planarity and Dye substituents that provide shields from radiant energy on azo chromophores, and which conferred good light fastness properties on the dyed substrate.

## CONCLUSION

Three different azo acid dyes were synthesised using 2-aminothiophene as a diazo component with Gamma acid, Tobais acid and J-acid as the coupling components. The colour of the dyes ranges from deep grey to deep blue, with characteristic melting points ranging from 195-210 °C. The percentage yield of the synthesised dyes ranges from 55% - 60%—all the dyes absorbed within the UV-visible region of the electromagnetic spectrum. The infra-red spectra of the synthesised dyes confirmed the presence of some chromophores such as NH/O-H, C=O, -N=N-, CN, Ar-H and S=O at varying vibrational frequencies, which accounts for the coloured nature of the synthesised dyes. The dyes exhibited very good to excellent fastness properties to wash and light when applied on polyester fibre.

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