



## SYNTHESIS AND DYEING PERFORMANCE OF MONOAZO ACID DYES DERIVED FROM 2-AMINO-THIOPHENE ON CHROME TANNED LEATHER AND NYLON 6,6 SUBSTRATE

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### ABSTRACT

*2-amino-thiophene and coupling with R, H, J and γ acid. Spectroscopic studies characterised the dyes. The dyeing capabilities were assessed by applying them on chrome-tanned leather and nylon 6,6 substrates. The dyes produced shades of red, dark blue and dark maroon. The synthesised dyes gave a maximum absorption within the UV-visible region with  $\lambda_{max}$  515-597 nm and molar extinction coefficient ranging from  $(3.217-4.221 \times 10^4 \text{ l/mol}^{-1} \text{ cm}^{-1})$ . The chrome-tanned leather gave a wash fastness rating ranging from 3(good), 4(very good) to 5(excellent), respectively. Nylon 6,6 gave a wash fastness rating ranging from 4(very good) to 5(excellent) fastness properties, and the light fastness properties of chrome-tanned leather gave a fastness rating of 4(moderate), 5(good), 6(very good) and 7 (excellent) and rubbing fastness rating 4(very good) to 5(excellent) on both substrates.*

### KEYWORDS

Monoazo dyes, synthesis, exhaustion, fastness properties, diazotization

### ARTICLE HISTORY:

Received: September, 2023

Received: in revised: October, 2023

Accepted: November, 2023

Published online: December, 2023

### INTRODUCTION

Azo-functionalised dyes bearing aromatic heterocyclic components (Towns, 1999) have attracted ever-increasing attention in recent years due to their range of colour, brightness, simplicity, ease of manufacturing, and good dyeing performance (Zhag *et al.*, 1997). Azo compounds are chemical components that are continually receiving attention in scientific research (Kirkan & Gub, 2008;

Otutu, *et al.*, 2011; Seferoglu, 2009). They are usually strong-coloured compounds that can be intensely yellow, red, orange, blue, green, etc., depending on the exact structure of the molecule.

These dyes have characteristically good tinctorial strength as well as stability. Their preparation procedures, by the classic diazotisation and coupling reactions, are very simple and of low cost. They have found wide application in the dyeing of protein fibres such as wool, angora, cashmere, and silk, as well as the milk protein fibre called "Silk Latte", the soy protein fibre called "Soy Silk", and the synthetic polyamide fibre nylon (Waheed & Ashrat, 2000; Dolaz & Yilmaz, 2009; Patel & Prajapati, 2012; Ehsan & Sebe, 2012). As a result of their colour, azo compounds are tremendously crucial as dyes and pigments for a long time (Otutu *et al.*, 2012). In fact, about half of the dyes in industrial use are azo dyes, which are mostly prepared from diazonium salt (Otutu *et al.*, 2012; Ebenso *et al.* 2008). Azo dyes account for over half of the dyes containing phenol as intermediates.

The study aimed to synthesise novel monoazo acid dyes and the assessment of their fastness properties on chrome-tanned leather and nylon 6,6 derived from 5-amino-4-cyano-2-methyl-N-phenylthiophene-3-carboxamide using coupling components such as R, H, J and  $\gamma$  acid.

## **MATERIAL AND METHODS**

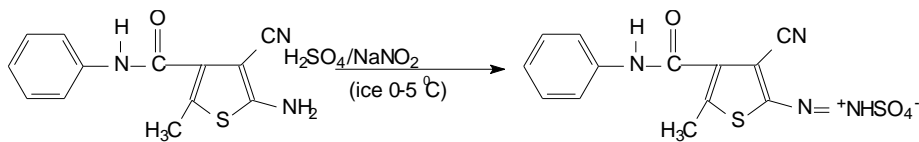
### **Materials**

All commercial products were purchased from Sigma-Aldrich. Such as H-acid, R-acid, J-acid. Gamma-acid, acetic acid, anionic detergent and all reagents are purified.

FT-IR spectrophotometer (Agilent CARRY 630 FT-IR Spectrophotometer), GC-MS spectrometry (7890B G.C. System).

### **Synthesis of dye diazonium salt solution (Zollinger, 2003)**

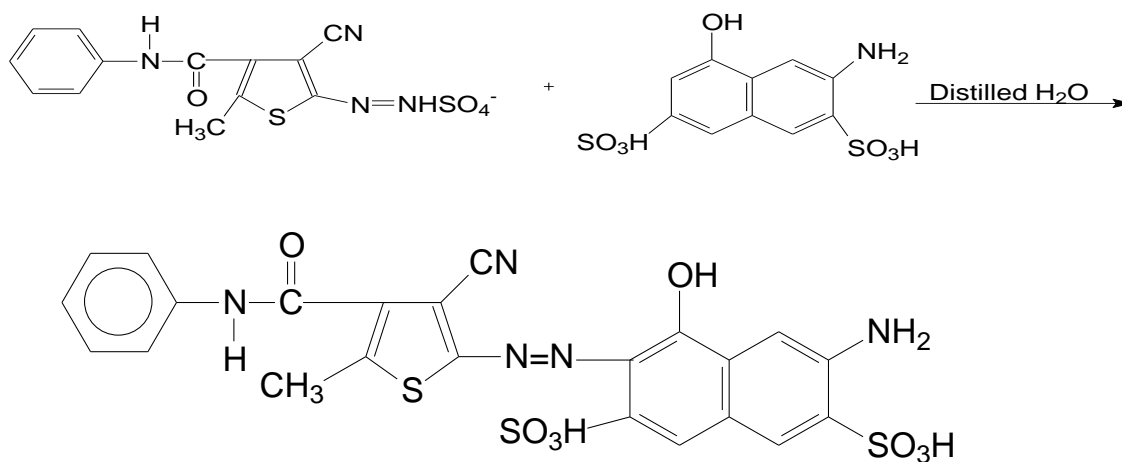
Sodium nitrite (1.38g, 0.02mol) was added portion-wise to a mixture of 10 cm<sup>3</sup> of nitrosyl sulphuric acid added to propionic acid and acetic acid 2:1 was cooled to 0-5°C in an ice bath and a mixture added to the (2.57g, 0.01) intermediate. The reaction mixture was then cooled to 0-5°C and added portion-wise, and stirring was continued for 2 hrs at 0-5°C to avoid excess heat that would destroy the diazonium salt. The resulting dye intermediate solution was obtained.



**Scheme 1:** Schematic route for the synthesis of diazonium salt

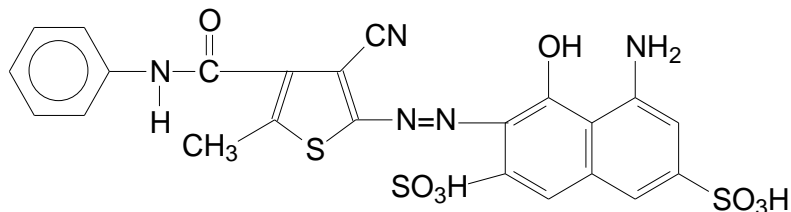
### Coupling of diazonium salt solution (Maradiya, 2010)

H-acid (2.0g, 0.01 mol) was dissolved in 10 cm<sup>3</sup> of distilled water, and the solution was cooled to 0-5°C. The freshly prepared diazonium salt solution was added dropwise over 45 minutes to the well-stirred solution, maintaining the temperature below 0-5°C with vigorous stirring. The stirring was done for 1 hour at 0-5°C, maintaining pH 4-5 using sodium carbonate solution (10% w/v). The resulting dye was collected, washed several times with water to ensure a free acid and dried in an oven at 40 °C. The result was repeated for R acid.



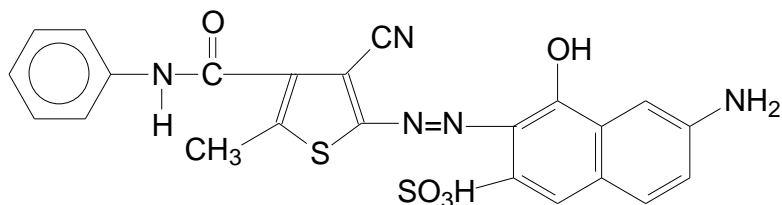
**Dye 1a**

3-amino-6-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)naphthalene-2,7-disulfonic acid



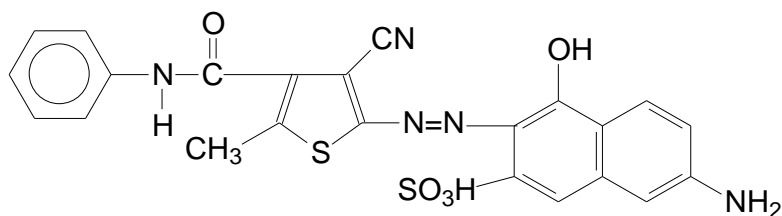
Dye 1b

5-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid



Dye 1c

6-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid



Dye 1d

7-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid

## Structures of Synthesised Dyes

### Dyeing of nylon 6, 6 fabric

For the nylon 6,6 fibre, a dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then heated in a 70°C bath and boiled within 15 minutes. Dyeing was carried out for one hour at 100°C with agitation. At the end of the dyeing process, the substrate was removed, squeezed and rinsed thoroughly under running tap water and allowed to dry at room temperature (Gregory, 1991).

## Dyeing of leather

Synthetic dyes were used to dye chrome-tanned leather. The standard method of dyeing leather was followed using the recipe.

- i. 120 % of water (60 °C)
- ii. 2 % of dye
- iii. 0.1 % of formic acid

A solution of the dye sample (2%) was made with distilled water using a heating mantle and was raised to 60 °C. The pH of the bath was adjusted to 5.5 with formic acid. The leather samples were introduced into the bath and run for 1 hour in a mechanical shaker at a controlled speed (Gregory, 1991).

## Application of dye solution

A solution was prepared by dissolving about 1g of dried dye powder in 100 ml of distilled water. The following parameter was utilised to determine the qualities required for the experiment.

$$\text{Number of ml of stock solution required} = \frac{W \times P}{C}$$

Where W = weight (in grams) of sample to be dyed

P = percentage of dye to be used

C = concentration (%) of stock solution (Choi *et al.*, 2008).

The general procedure of dyeing chrome-tanned leather

1 % of dye (on the weight of the materials)

50 + 2°C dyeing temperature

0.1 % of formic acid on the weight of the dye

Time of dyeing: one hour

Liquor ratio 20:1

## Determination of dye bath exhaustion

Each substrate's percentage dye bath exhaustion (%E) was calculated using the equation below.

$$\% E = \frac{A_0 - A_1}{A_0} \times 100$$

$A_0$  and  $A_1$  are the absorbance at  $\lambda_{\max}$  of the dye bath before and after dyeing, respectively.

### Fastness Properties of the Substrate

Light, wash and rub fastness of dyed substrates according to SLT 401 (IUF 401) by the standard greyscale and rub fastness tester (Machine Model S.T.M.), respectively.

## RESULTS AND DISCUSSION

**Table 1:** Physical properties of the synthesised dye intermediate

Name of intermediate	Colour	Melting point (°C)	Percentage yield (%)	Molecular weight (g/mol)	Molecular formula
2-amino thiophene	Dark brown	188-194	97	257	C <sub>13</sub> H <sub>11</sub> ON <sub>3</sub> S

**Table 2:** Physical properties of the synthesised mono azo acid dyes

Dye no	Molecular formula	Shade crystal	Molecular weight(g/mol)	Melting point (°C)	Percentage yield (%)
1a	C <sub>23</sub> H <sub>17</sub> O <sub>8</sub> S <sub>3</sub> N <sub>5</sub>	Red	587	200-202	76
1b	C <sub>23</sub> H <sub>17</sub> O <sub>4</sub> S <sub>3</sub> N <sub>5</sub>	Dark blue	587	191-194	62
1c	C <sub>26</sub> H <sub>17</sub> O <sub>5</sub> S <sub>2</sub> N <sub>5</sub>	Dark maroon	507	120-122	68
1d	C <sub>26</sub> H <sub>17</sub> O <sub>5</sub> S <sub>2</sub> N <sub>5</sub>	Red	507	212-214	82

**Table 3:** Spectra data of the synthesised mono azo acid dyes using dimethylformamide and ethanol

Dyes no	$\lambda_{\max}$ in (nm) D.M.F.	$\lambda_{\max}$ in (nm) Ethanol	Molar Extinction Coefficient in(DMF) x 10 <sup>4</sup> (l/mol <sup>-1</sup> cm <sup>-1</sup> )
1a	530	515	4.181
1b	597	572	4.176
1c	580	577	3.217
1d	565	527	4.145

### The spectral data analysis of synthesised monoazo acid dyes

The synthesised monoazo acid dye, as shown in Table 3, was absorbed at 530, 597, 580, and 565 nm, respectively, in dimethylformamide. Dye 1b, for instance, is more bathochromic than dyes 1a, 1c, and 1d. Dye 1b was synthesised from 8- amino-1- naphthol 3-6-disulfuric acid coupling component. This is followed by dye 1c containing 2, amino-8-naphthol sulfuric acid as coupling component, which is absorbed at 580nm and is a bathochromic compound with dye 1a and 1d, [NIJOSTAM Vol. 1(1) December, 2023, pp. 207-216. www.nijostam.org]

which are absorbed at 530 and 565 nm containing 2-naphthol-3-6 disulfuric acid and 2-amino-5-naphthol-7-sulfuric acid respectively,

The substituent shifts of maximum wavelength ( $\lambda_{\max}$ ) absorption to shorter wavelength, with reduced absorbance energy, intensified the colour of dyes. The colour change observed for each dye is due to electrons' oscillation and additional substituents. Maximum absorption moves to longer wavelengths as the amount of delocalisation increases. Therefore, the maximum absorption moves to a shorter frequency, the absorption needing less energy gap between the bonding and anti-bonding orbitals (Choi *et al.*, 2008).

**Table 4:** Infrared spectra of mono azo acid dyes

Functional group	OH & NH	Aromatic C-H	Carbonyl C-O	Aromatic amine C-N	Azo N=N
Types of vibration	Stretching	Stretching	Stretching	Stretching	Stretching
1a	3347.1		1636.3	1315.8	1488.6
1b	3377.0		1636.3	1367	1499.4 1529.2
1c	3373.2		1703.4 1654.9	1319.5	1468.5
1d	3410.5		1636.3		1535.7 1468.6

#### Assessment of FT-IR group absorption spectroscopic properties of synthesised acid dye

It was pronounced, as shown in Table 4, that dye 1a to d were obtained by diazotisation of 2-aminothiophene and coupling with 2-naphthol-3-6 disulfuric acid, 8-amino-1-naphthol-3-6, disulfuric acid, 2-amino-8-naphthol sulfuric acid and 2-amino-5-naphthol-7 sulfuric acids respectively. The absorption peaks due to (O-H and N-H) group at 3347  $\text{cm}^{-1}$ , (C=O) at 1636.3  $\text{cm}^{-1}$ , (C-N) at 1315.8  $\text{cm}^{-1}$ , and (-N=N-) group at 1488.6  $\text{cm}^{-1}$ , stretching vibration in dye 1a.

Dye 1b, which is obtained by diazotisation of diazonium salt coupling with 8-amino-1-naphthol-3-6-disulfuric acid showed absorption peaks due to (O-H and N-H) group at 3377.0  $\text{cm}^{-1}$ , (C=O) group at 1636  $\text{cm}^{-1}$ , (C-N) at 1367 $\text{cm}^{-1}$ , and (-N=N-) group at 1499.4 and 1529.2 $\text{cm}^{-1}$ , stretching vibration.

Dye 1c, which is obtained by coupling diazonium salt with 2-amino-8-naphthol sulfuric acid gave absorption peak due (O – H) and N – H group at  $3373.2\text{cm}^{-1}$ , (C=O) group at  $1703.4\text{cm}^{-1}$ , and  $1654.9\text{cm}^{-1}$ , (C–N) group at  $1319.5\text{cm}^{-1}$ , and (N=N) group at  $1468.5\text{cm}^{-1}$  stretching vibration.

Dye 1d, which was obtained by coupling diazonium salt with 2-amino-5-naphthol-sulfuric acid, showed an absorption peak due to (O – H and N – H) group at  $3410.5\text{cm}^{-1}$ , (C = O) group at  $1636.3\text{cm}^{-1}$ , (-N=N-) group at  $1535.7\text{cm}^{-1}$ , and  $1468.6\text{cm}^{-1}$ , stretching vibration.

**Table 5:** Light and wash fastness properties of chrome-tanned dyed leather

Dyed no	Light fastness rating	Wash fastness rating
1a	5-6	4-4
1b	5	4-5
1c	5-6	4-5
1d	3-4	3-4

**Table 6:** Rubbing fastness properties on chrome-tanned dyed leather

Dyed no	number of rubs	Fastness rating	Staining of adjacent un-dyed cotton
1a	100	5	4
1b	100	5	4
1c	100	5	3
1d	100	5	3

Tables 6 shows the wash fastness of the dyes coupled with diazonium salt, 2-naphthol, 3-6 disulfonic acid, 8-amino-1-naphthol, 3-6. Disulphonic acid, 2-amino-8-naphthol sulphonic acid and 2-amino -5- naphthol -7- sulphonic acid. These dyes gave purple, brown, pink, and deep blue to khaki hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the substrates ranging from good (3), very good (4) to excellent (5).

Dye 1a-1d gave a wash fastness rating on chrome tanned leather (3-5) good, very good and excellent, which is attributed to dyed being challenging to wash out, while nylon 6,6 gave a wash fastness rating (3-4) good to very good. It could be seen that chrome-tanned leather gave better wash fastness than nylon 6,6. This could result from the fabric's texture, which in nylon 6,6

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involved high diffusion and penetration, and in chrome-tanned leather, its interweave involved slow diffusion and penetration.

## CONCLUSION

A series of new monoazo acid dyes have been synthesised in moderate yield by diazotising 2-amino-thiophene and coupling with R, H, J and  $\gamma$  acid. Spectroscopic studies characterised the dyes. The dyeing capabilities were assessed by applying them on chrome-tanned leather and nylon 6,6 substrates. The dyes were found to produce shades of red, dark blue and dark maroon. The synthesised dyes gave a maximum absorption within the UV-visible region with  $\lambda_{\max}$  515-597 nm and molar extinction coefficient ranging from  $(3.217-4.221 \times 10^4 \text{ l/mol}^{-1} \text{ cm}^{-1})$ . The chrome-tanned leather gave a wash fastness rating ranging from 3(good), 4(very good) to 5(excellent), respectively and nylon 6,6 gave a wash fastness rating ranging from 4(very good) to 5(excellent) fastness properties, and the light fastness properties of chrome tanned leather gave a fastness rating 4(moderate), 5(good), 6(very good) and 7(excellent) and rubbing fastness rating 4(very good) to 5(excellent) on both substrates.

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