

Original Article

Synthesis and Characterization of Acid Dyes Based on Substituted Pyridone Using Metal Complexes (1:2) and Study of their Application on Nylon Fabrics (6.6)

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ABSTRACT

In this study, the synthesis of acid dyes was investigated from 4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone and their pyridone derivatives, followed by their metal complexes (Fe (II) and Cu (II)). The pyridone derivatives comprise 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone and 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone. The acid dyes were successfully synthesized with good yield ranging from 75-96% and were metallized using Fe (II) and Cu (II) in the ratio 1:2. Metallized acid dyes using Fe (II) and Cu (II) were successfully synthesized with good yield ranging from 82-96%. Characterization of these dyes structure was established by FTIR, UV, and GCMS. To learn more about these acid dyes' dyeing capabilities, they were applied to nylon 6.6 fabrics. All of these acid dyes produced hues of yellow, greenish yellow, dark grey, and brown. On nylon 6.6 fabrics, the washing fastness was moderate to excellent (4-7), the rubbing fastness was good to excellent in both wet and dry conditions (3-5), and perspiration fastness was moderate to very good (3-4). Due to the high tinctorial strength and effective exhaustion of metallized dyes on nylon 6.6 fabrics when pH is 5 and non-metallized acid dyes are used, non-metallized acid dyes' fastness qualities were lower than those of metal complex acid (1:2) dyes.

Introduction

A dye is an organic substance that is colored and absorbs light significantly in the visible spectrum. It can firmly adhere to fibers due to chemical and physical bonds between the dye's

molecular groups and those on the fiber. A dye should react quickly to light, rubbing, and water in order to be of commercial value [1].

A compound's color is connected to its chemical makeup [2]. Witt's theory (1976), which asserts that there is a connection between color and

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chemical composition of a compound and that a dye is composed of two parts, is one theory that attempts to explain the relationship between color and chemical composition of a substance: chromophore and auxochromes. Witt claims that if an organic substance has specific unsaturated groups, color will typically be present. The groups are referred to as chromophores (*e.g.* azo $N=N$, carbonyl $>C=O$ etc.).

Azo functional dyes bearing aromatic heterocyclic component are non-naturally occurring nitrogen compounds continuously receiving attention in scientific research [3-6]. Azo dyes constitute the largest group of azo compounds and the most widely used colorants in the industry. Several derivatives of pyrazole (azo) were the focus of analysis owing to a range of applications. The uses of the azo dyes comprise their use in coloring fibers, owing to their affinity for Nylon 6.6 and silk [7], photoelectronics [8], and printing systems [9, 10] as well as in analytical [11, 12] and food chemistry [13]. Furthermore, several azo compounds have been synthesized with relevant industrial and medical goal [14, 15].

Azo dyes are the biggest category of synthetic dyes that contribute 60-70% of the entire production synthetic dyes being presently employed. Wide range utility and synthesis of azo dyes is owing to their high molar extinction coefficient, medium to high fastness, high solubility, high substantivity, diversity in structures, easy handiness of raw materials, and simple synthetic procedures [16-18]. There are several categories of azo dyes like reactive dyes, direct dyes, vat dyes, and metal complex dyes. Among these totally different categories of dyes, direct dyes are straightforward to spread on and synthesize [19, 20]. Direct dyes are useful on cotton and nylon fibers in medium that are neutral or slightly alkaline. Various types of nylon with two most common for textile and plastics industries are nylon 6, and nylon 6.6. The latter is made of two monomers, each containing 6 carbon atoms hexamethylenediamine and adipic acid, which gave nylon 6.6 its name [21].

Experimental

Materials and methods

The substances used to make the colors were of analytical quality and used without further purification. The ingredients were purchased from Sigma Aldrich. The open capillary method was used to calculate melting points using a Gallenkamp melting point apparatus. The visible absorbance was measured with a UV-Visible spectrophotometer (Agilent technologies). FTIR (SHIMADZU FTIR-8400S) and the dyeing were carried out using KMS-IRE Laboratory Dyeing Machine –Elite.

Synthesis of acid (pyridone) dyes

The process simply involves nitrosation of 4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone, reduction, diazotization, coupling, and metallization. Four main dyes were synthesized using the same diazotization procedure, different coupling component. The synthesis involves the coupling components which are 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, and 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone. Likewise, metallization was done using Cu (II) and Fe (II).

Nitrosation and reduction of 4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone

1-(*p*-Sulfophenyl)-3-methyl-5-pyrazolone (**1**) (5.08 g, 0.1 mol) was suspended in H_2O (50 ml). Hydrochloric acid (9 ml) was added to this well stirred suspension in a beaker on a magnetic hotplate stirrer. In an ice bath, the reaction mixture was cooled to 0 to 5 °C. Over the course of 35 minutes, while stirring, a solution of $NaNO_2$ (5.38 g, 0.1 mol) in water (5 ml) that had previously been chilled to 0 °C was added. An hour of continuous stirring at the same temperature resulted in a positive nitrous acid test. The extra nitrous acid was then removed using the exact quantity of sulphamic acid. The salting out procedure was completed before the nitroso (oxime) was filtered out. The oxime was

then reduced by stirring in 40 ml of water for 4 hours while it was boiling with 17 ml of HCl and 4.6 g of zinc metal. After the reaction was complete, 6N NaOH was added to the reaction liquid to elevate the pH to 9, which precipitated the 1-(*p*-methylphenyl)-3-methyl-4-amino pyrazolones [22].

Diazotization and coupling with pyridone derivative

Concentrated HCl (0.7 ml) and sodium nitrite solution were added to the well-stirred beaker containing aqueous solution in an ice bath (0.538 g) of 1-(*p*-sulphophenyl)-3-methyl-4-amino pyrazolone (at 0-5 °C) (0.14 g in 2 ml H₂O). To produce the 1-(*p*-sulphophenyl)-3-methyl-4-amino pyrazolone diazonium salt, the reaction mixture was rapidly rotated for an hour at the aforementioned temperature [22]. The resulting diazonium compound was coupled to several of the couplers mentioned before to make our dyes. Thus, 0.538 g (0.01 mol) 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone (**4a**) was dissolved in 2.564 ml water containing 0.538g NaCO₃ and coupled with prepared diazo. 2-3 hours were allowed to the reaction mixture to finish coupling at 30-35 °C [23]. It was cooled to bring the dye to room temperature. Its pH was adjusted by HCl to 4.5 before filtering. The cake was baked at 50 °C until it reached a steady weight. As illustrated in the following chemical scheme, additional dyes **6b-6d** were made from couplers **5b-5d** using the same method.

Metallization of acid dyes

0.54 g (0.005 mol) of dye **6a** was reduced with HCl to a pH of 6.5 to synthesize metal complexes (iron complex). Then, it was heated to 65-70 °C while being stirred with a magnetic hot plate stirrer, and dropwise additions of 5 ml (0.005 mol Fe²⁺) of ferrous sulfate (FeSO₄•7H₂O) solution were made. For an additional 4-5 hours, stirring and heating were maintained at this temperature to finish the metallization. The dye was cooled to room temperature, and concentrated HCl was used to bring its pH down to 1.0. After being salted with sodium chloride and filtered through paper, it was dried in an

oven at 50 °C until it reached a consistent weight.

Similarly, CuSO₄•5H₂O treatment of dye with a mole ratio of 1:2 of metal to ligand led to the formation of copper (II) complexes of dye **6a**. Complexes **8a-8h** were created in this manner using the appropriate dye ligands. The two metal complexes of dye **6a**, Cu(II) and Fe(II), were also created by treating them with FeSO₄•7H₂O at 65-70 °C with a metal to ligand mole ratio of 1:2.

Complexes **8a-8h** were created through this technique using the corresponding dye ligands (**Scheme 1**).

Dyeing method

Dyeing of Nylon 6.6

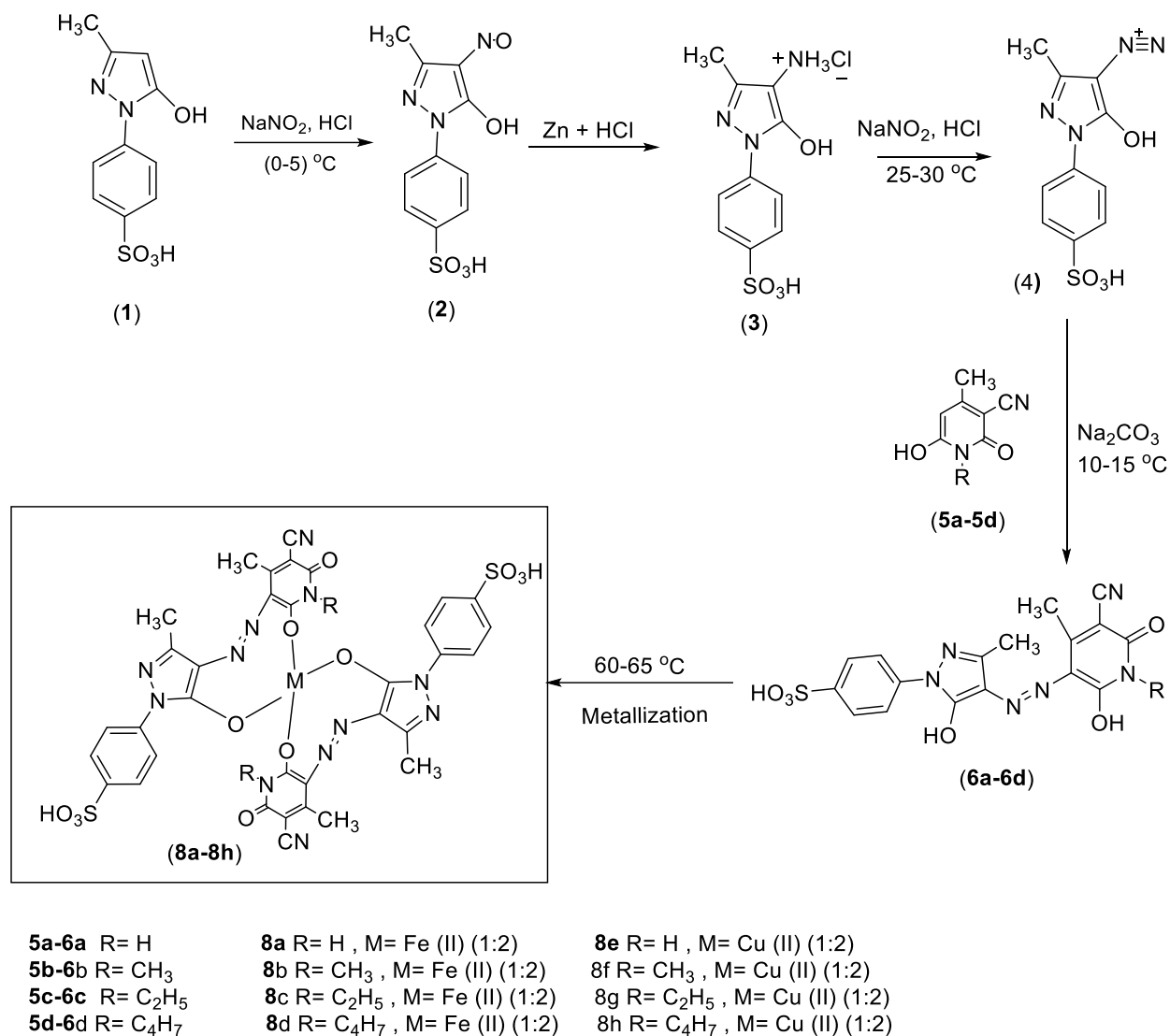
The dye bath was made with a 50:1 liquor to liquor ratio and 2% color by weight of fabric. 2 ml acetic acid was added to the dye bath, and pH was raised to 5 [24].

2 ml addition of acetic acid was added after the pH of the dye bath was brought down to 5. The excess water was squeezed out after 1 g of dyed nylon 6.6 had been soaked in water for 5 minutes. The wet fabric was then placed in the dye solution on a control steam bath, where the temperature was initially set at 80 to 90 °C, and then gradually increased to boil over 60 minute while agitating the sample. It takes 1 h for dyeing to complete at boil. After the fabric had finished being dyed, it was removed, properly cleaned with cold water, and allowed to air dry [24-26].

Results and Discussion

Synthesis and spectrum analysis of pyridone acid dyes and their metal complexes

The iron (Fe, II) and copper (Cu, II) complexes of acid dyes were created in a five-step process, as illustrated in the reaction (**Scheme 1**). According to Knorr's instructions, SPMP [1-(4-sulphophenyl)-3-methyl-2-pyrazolin-5-one] was nitrosated at 0-5 °C using NaNO₂ and HCl. The nitroso compound was filtered to remove some terry material. The common salt salted out the cleared nitroso derivative, which



Scheme 1. Synthesis of ligand acid dyes **8a-8d** and their Fe (II); Cu (II) complexes (**8e-8h**)

typically occurs as an oxime (as shown by its FTIR). It was filtered, and then dried.

Utilizing zinc and HCl, oxime was reduced at 100-105 °C. The boiling HCl solution received a series of little additions of the zinc and oxime⁽¹²⁾. The solution lost its hue, signaling the end of the reduction. To avoid aerial oxidation during cooling, some more zinc dust was also added. The amine hydrochloride that resulted was cooled to -7 °C.

To avoid the formation of rubazoic acid, which is automatically formed during this reaction with increasing temperature due to the oxidizing action of nitrous acid, formed *in situ*,

this amine hydrochloride was diazotized using an aqueous solution of NaCO₃ (26.9 g dissolved in 12.82 ml of solution) and HCl at -5 to -2 °C. The resulting diazonium salt was mixed with several para substituted pyridones, 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, and 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone. At a pH of 8 to 9, an alkaline medium was used for the coupling. Following the result of reaction, the pH of the solution was reduced with HCl to 1.0 in order to precipitate the produced dyes **6a-6d**.

The filtered dyes were dried and ethanol-purified. These dyes were metalized by adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to their alkaline solution and heating it to 65–70 °C. Taking the TLC of the reaction mixture in 9:1 chloroform and methanol allowed us to observe that the metallization took about 4–5 hours to complete. The addition of HCl precipitated the dyes (**8a–8h**), which were then filtered and dried at 80 °C in an oven. Once more, the ethanol was removed from these hues, they were dried, weighed, and the % yield was determined. The un-metallized dyes 6a–d, which are tridentate ligands, stoichiometrically mix in a 1:2 ratio with the metals iron (Fe, II) and copper (Cu, II) in the aforementioned chemical scheme to create complexes. While the other three coordination numbers of these metals have been satisfied by three water molecules, the

lone pairs of electrons in the case of the Fe^{2+} and Cu^{2+} complexes are provided by two oxygen atoms and one nitrogen atom of the diazo linkage. These dyes' **8a–8h** UV-Vis spectrophotometric investigations have supported the complicated production pattern. Different moieties in the compounds' IR spectra displayed stretching and bending bands typical of the synthetic compounds. The metal complexes and produced acid dyes' infrared spectra showed absorption peaks as a result of O-H str, C-H str. Aliphatic, C-H₃ str, CN str, C=O str, N=N str, S=O str, C=C str, and O-M str with stretching and bending at 3634, 3086; 2939; 2222; 1712; 1527; 1303; 1612; and 771, respectively, are depicted from the FTIR spectra (**Figure 1**). 3610; 3086; 2906; 2222; 1712; 1573; 1357; 1697 and 745 respectively, are depicted from the FTIR spectra (**Figure 2**).

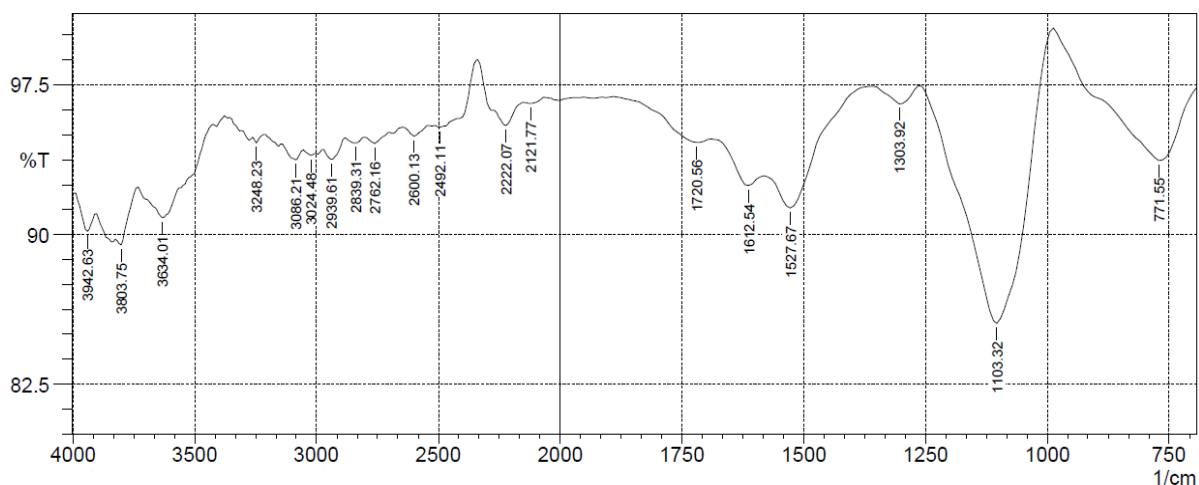


Figure 1. FTIR spectrum of Cu (1:2) of dye **8e**

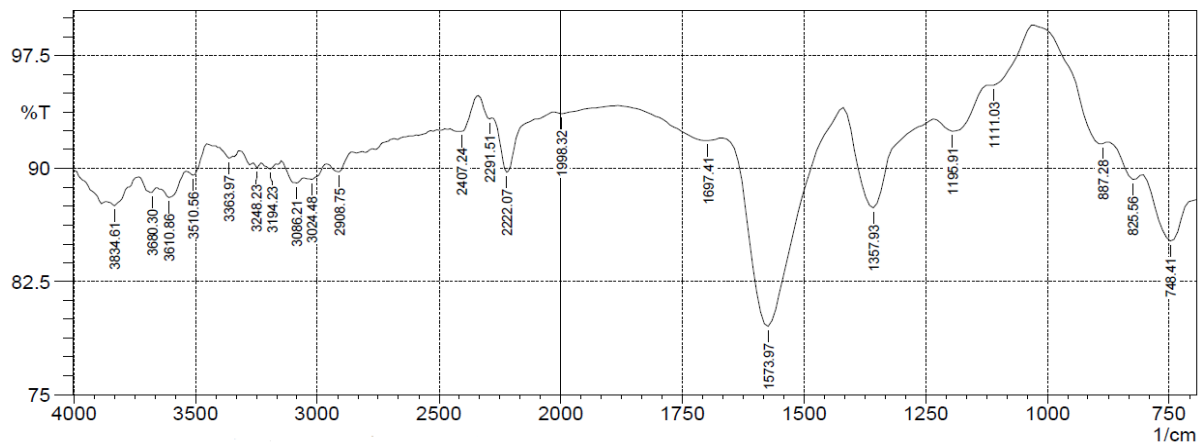


Figure 2. FTIR spectrum of Fe (1:2) of dye **8a**

Table 1. The Wavelength of maximum absorption and molar coefficient of the dyes

Dye	E _{max} in Ethanol 10 ⁴ Lmol ⁻¹ cm ⁻¹	Ethanol λ _{max} (nm) a	Ethanol+ HCl λ _{max} (nm) b	Dist. H ₂ O λ _{max} (nm)	Change in λ _{max} (nm) (b-a)
6a	2.71	434	434	434	0
6b	4.16	416	413	413	16
6c	3.24	434	430	433	-4
6d	1.13	434	432	428	-2
8e	7.92	413	412	434	-1
8a	5.75	434	593	433	159
8f	5.47	413	412	428	-1
8b	6.13	422	433	422	11
8g	4.68	421	434	431	3
8c	4.88	437	431	433	-6
8h	5.97	450	425	429	-25
8d	5.98	433	434	421	1

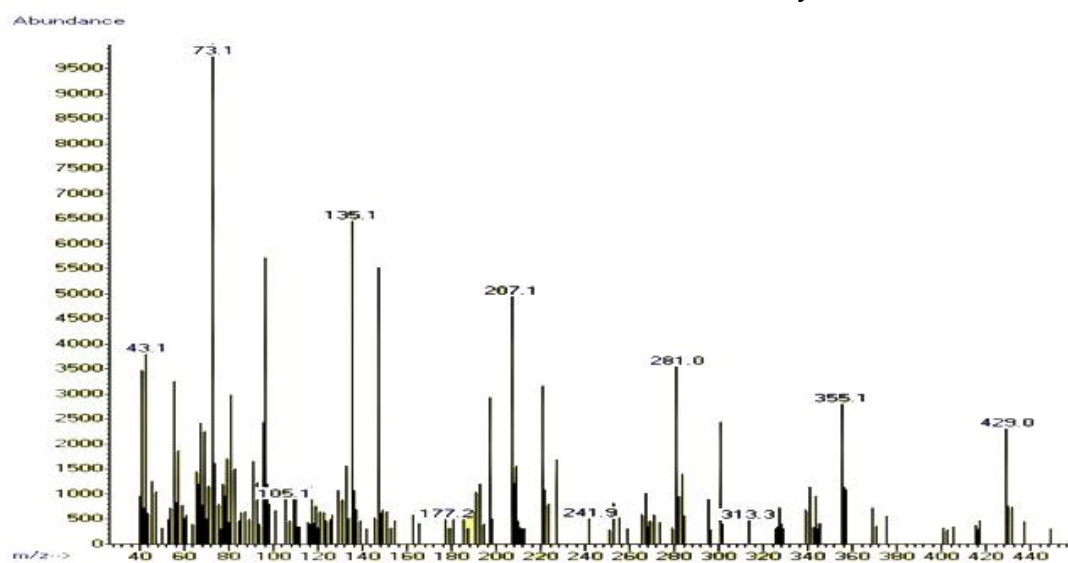
The mass spectrum of dye D1 gave mass-to-charge ratio (m/z) of 77, 148, 158, 254, 282, and parent 445 representing molecular ion (m) and the corresponding positive charge fragment of C₆H₅⁺, C₈H₇N₂O₂⁺, C₆H₆O₃S⁺, C₁₀H₁₀O₄S⁺, C₁₀H₁₀N₄O₄S⁺, and C₁₇H₁₅N₆O₆S⁺, are demonstrated respectively in **Figure 3**.

UV-Visible spectral of dyes

The thorough UV-Visible analysis of dyes revealed that, in accordance with the well-

known UV-Visible absorption pattern of compounds, metal complexes of ligand dyes possessing electro-withdrawing group electrons displayed hypsochromic shift, while those bearing electron-donor groups displayed bathochromic shift in absorbance [22].

After the development of a metal complex, the ability of d-orbitals to absorb or donate electrons, whether large or tiny, determines how colored the dyes change [27]. Wavelength of the maximum absorption and molar coefficient of the dyes are listed in **Table 1**. This

**Figure 3.** GCMS of synthesized MP dye (6b) with pyridone coupling component.

largest shift in iron (II) complex is attributed to three unpaired electrons in 3d orbitals. Being highly paramagnetic complex, there is small energy gap between t_{2g} and e_g orbitals. Similarly copper (II) complex dyes expressed different colors after complex formation [28].

Physical characteristics of synthesized dyes

The physical characteristics of dyes are presented in **Table 2**. Each of the different dyes synthesized possessed unique physical characteristics. They have well-defined melting points (342-438 °C), yield point, and molecular mass characteristics of pure compounds.

Fastness Properties

The washing fastness of all these dyes showed good to excellent, light fastness showed moderate to excellent (4-7), rubbing fastness indicate good to excellent in wet and dry (3-5), and fastness to perspiration showed good to excellent (3-5) on nylon 6.6 fibers. The fastness properties values of the dyes are provided in **Table 3** (light and wash fastness), **Table 4** (rubbing fastness properties), and **Table 5** (fastness to perspiration), respectively.

In addition, shade of dyes **6a-6d**, **8a-8d**, and **8e-8h** on nylon 6.6 fabric are illustrated in the **Figure 4**.

Table 2. Physical characteristics of acid dyes based on pyridone derivatives

Dye(Molecular Formular)	Molecular Mass (gmol ⁻¹)	Melting Point (° C)	Yield (%)	Color of Crystal
6a (C ₁₇ H ₁₄ N ₆ O ₆ S)	430	342-344	75	Yellow
6b (C ₁₇ H ₁₇ N ₆ O ₆ S)	445	345-347	95	Yellow
6c (C ₁₉ H ₁₉ N ₆ O ₆ S)	460	304-306	90	Yellow
6d (C ₂₁ H ₂₃ N ₆ O ₆ S)	488	310-312	96	Yellow
8e (C ₃₄ H ₂₄ CuN ₁₂ O ₁₂ S ₂)	919	430-432	93	Deep Brown
8a (C ₃₄ H ₂₄ FeN ₁₂ O ₁₂ S ₂)	912	336-338	91	Brown
8f (C ₃₆ H ₂₈ CuN ₁₂ O ₁₂ S ₂)	949	410-412	92	Black grey
8b (C ₃₆ H ₂₈ FeN ₁₂ O ₁₂ S ₂)	942	411-412	91	Black grey
8g (C ₃₈ H ₃₂ CuN ₁₂ O ₁₂ S ₂)	979	355-357	90	Deep brown
8c (C ₃₈ H ₃₂ FeN ₁₂ O ₁₂ S ₂)	972	411-414	80	Deep brown
8h (C ₄₂ H ₃₆ CuN ₁₂ O ₁₂ S ₂)	1035	436-438	92	Green
8d (C ₄₂ H ₃₆ FeN ₁₂ O ₁₂ S ₂)	1028	436-437	91	Yellow

Table 3. Fastness properties of the synthesized dyes on Nylon 6.6

Dye code	Fastness	
	Light Nylon 6.6	Washing Nylon 6.6
6a	7	3
6b	4	3
6c	5	3
6d	6	3
8e	5	3
8a	6	3
8f	4	3
8b	6	4
8g	4	3
8c	6	3
8h	4	3
8d	6	3

Table 4. Rubbing fastness properties of the synthesized dyes on Nylon 6.6

Dye code	Rubbing Fastness	
	Dry Nylon 6.6	Wet Nylon 6.6
6a	4-5	4-5
6b	4-5	4-5
6c	4-5	4-5
6d	4-5	4-5
8e	4-5	4
8a	4-5	4
8f	4-5	4
8b	4-5	4
8g	4-5	4
8c	4-5	4
8h	4-5	4
8d	4-5	4

Table 5. Fastness to perspiration properties of the synthesized dyes on Nylon 6.6

Dye code	Fastness to Perspiration	
	Acid Nylon 6.6	Alkaline Nylon 6.6
6a	4	4
6b	4	4
6c	4	4
6d	4	4
8e	3	4
8a	4	4
8f	3	3
8b	3	3
8g	3	3
8c	3	3
8h	4	4
8d	4	4

**Figure 4.** Shade of dyes 6a-6d, 8a-8d, and 8e-8h on nylon 6.6 fabric

Percentage (%) exhaustion of synthesized dyes

The synthetic dyes' percentage (%) dye exhaustion on Nylon 6.6. is displayed in **Figure 5**.

Effect of pH on dye exhaustion

The effect of pH on dye exhaustion (%) is carried out on nylon 6.6 fabrics, as shown in **Figure 6**.

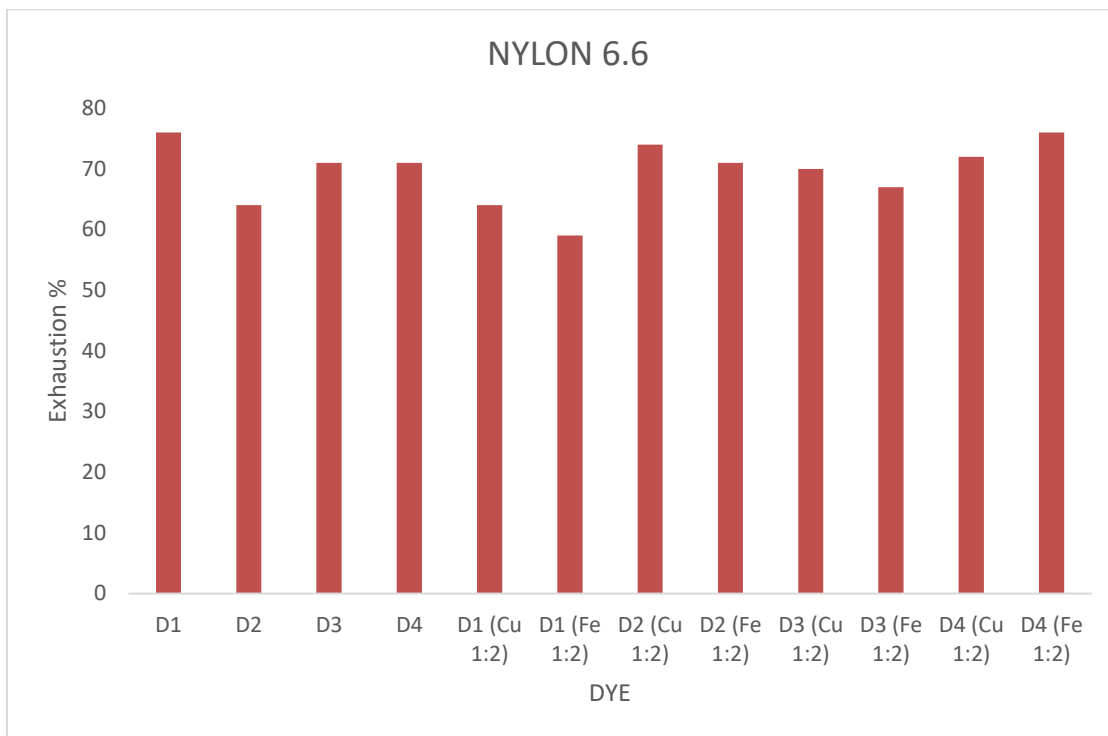


Figure 5. Percentage (%) exhaustion of synthesized dyes on nylon 6.6.

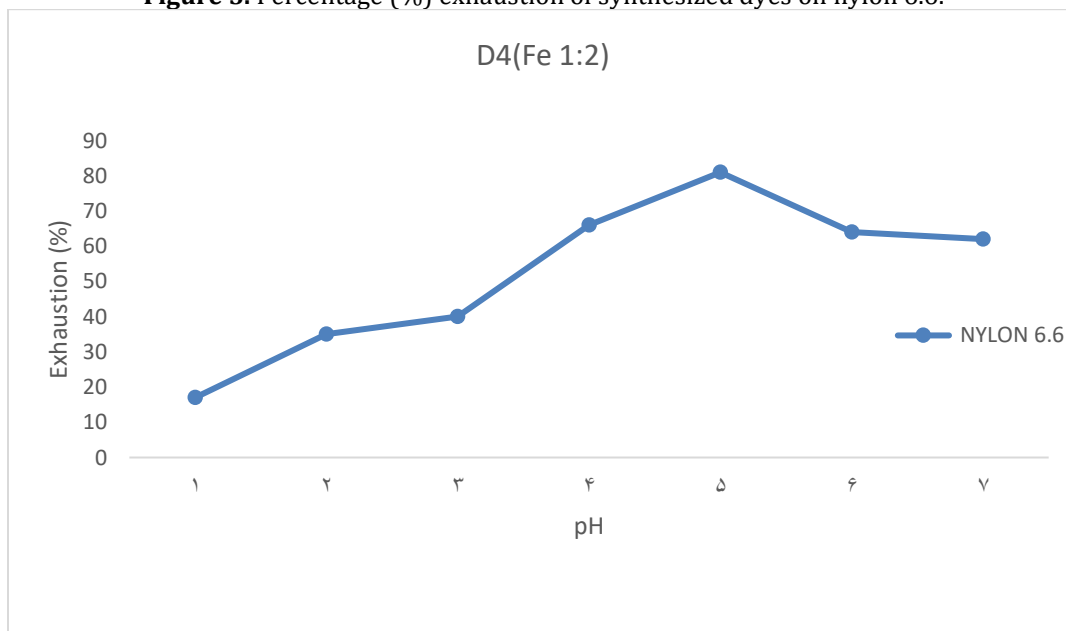


Figure 6. Effect of pH on dye exhaustion showed nylon 6.6 have pH at 5

Table 6. Previous report of acid dyes used in nylon fabrics

Previous Report	Application on Nylon Fabrics Result	Remark
Studies on the Dyeing Of Wool and Nylon Fabrics with Some Acid Dyes [29]	Relatively, nylon showed higher percentage exhaustion compared to wool. Likewise, the dyed wool and nylon fabrics possess good fastness towards bleaching rubbing, pressing, and perspiration, but poor fastness to higher and washing.	Nylon shows higher %exhaustion, good fastness properties, and high light fastness.
Effect of Tannic Acid on the Dyeing Process of Nylon 6 Fabric with Cationic Dye [30]	The washing and rubbing fastness of nylon 6 fabrics dyed with the emulsion system are generally very good. Interestingly, the fixation can reach 90-95% in the emulsion system after adding an anionic crosslinking fluorescent whitening agent, Uvitex RSB. The perspiration fastness shows good improvement, especially in the acidic medium.	Perspiration, washing, and rubbing fastness are good
Inhibitive Effect of NaCl and Citric Acid on the Color Yield of Acid Dye on Nylon Fabric [31]	The adsorption mechanism of acid yellow 23 dye was studied using 5% sodium chloride and 1% acid concentration at 50 °C dyeing temperature.	Anything that affects dye substantivity, absorption, and/or exhaustion will definitely affect color yield of such a dye.
Laccase-catalysed coloration of wool and nylon [32]	The results also demonstrate the ability of laccase as a novel and creative tool for the enzymatic process to permit effective surface patterning through controlled applications for shadow and contrast colored effects. The opportunities discussed could provide the textile industry with realistic and viable options to use enzyme-based surface patterning with the potential of moving towards sustainable development.	The use of varied buffer systems, pH values, and aromatic compound concentrations proved the most beneficial for increasing the range of possible colors. Previously unreported colors such as pink, green, and blue were achieved. Color fastness of the enzymatically dyed wool and nylon fabrics was evaluated, resulting in reasonable good color fastness to wash, but poor fastness to light.

Also, previous report of acid dyes used in nylon fabrics is summarized in the **Table 6**.

Conclusion

With the help of novel acid dyes created by starting with p-sulphophenyl-3-methyl-5-pyrazolone, the problem of colors with inferior tinctorial strength and fastness capabilities in textile dyeing has been solved which were transformed from 1-(p-methylphenyl)-3-methyl-4-amino pyrazolones through diazotization and coupling with 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone, 1-ethyl-2-hydroxy-4-methyl-5-

cyano-6-pyridone, and 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone into non-metal complex acid dyes. These non-metal complex dyes undergo metallization with Fe (II) and Cu (II) ions resulting in the metal complex dyes. The synthesized acid and metallic dyes were applied on nylon 6.6 fabrics best at pH 5 [33, 34].

All the dyes gave yellow, greenish yellow, dark grey, and brown colored shades. The synthesized dyes have high tinctorial strength, and good color fastness to washing, light, rubbing, and perspiration, indicating the existence of strong bonds (ionic bonds) between the dye and fabrics. Exhaustion of the

dyes is very good which indicates that the dyes have good affinity for the nylon (6.6) fabrics.

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References

- [1]. N.N. Mahapatra, Textile Dyes, Woodhead Publishing India, **2016**, 81-96. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [2]. R.C. Gurdeep, Synthetic Dyes, Himalaya Publishing House Mumbai, **2009**, 342. [[Google Scholar](#)], [[Publisher](#)]
- [3]. H.R. Maradiya, V.S. Patel, *J. Serb. Chem. Soc.*, **2002**, 67, 17-26. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [4]. B. Kirkan, R. Gup, *Turk. J. Chem.*, **2008**, 32, 9-17. [[Google Scholar](#)], [[Publisher](#)]
- [5]. J.O. Otutu, *Int. j. res. rev. appl. sci.*, **2013**, 15, 292-296. [[Google Scholar](#)], [[Publisher](#)]
- [6]. Z. Seferoglu, *Arkivoc*, **2009**, 7, 42-57. [[Google Scholar](#)], [[Publisher](#)]
- [7]. D.R. Patel, K.C. Patel, *Fibers Polym.*, **2011**, 12, 741-752. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8]. N. Sekar, Ecofriendly metal complex dyes- An update. *Colourage*, **1999**, 46, S63-65. [[Google Scholar](#)]
- [9]. T. Abe, S. Mano, Y. Yamaya, A. Tomotake, *J. Imaging Sci. Technol.*, **1999**, 43, 339-344. [[Google Scholar](#)], [[Publisher](#)]
- [10]. V. Dharmalingam, A.K. Ramasamy, V. Balasuramanian, *J. Chem.*, **2011**, 8, S211-S224. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [11]. N.A. Abdalla, M.T. El-Haty, F.A.E. Adam, F.W. Hassan, *Rev. Roum. Chim.*, **2013**, 58, 899-913. [[Crossref](#)], [[Google Scholar](#)]
- [12]. A.S. Amin, T.Y. Mohammed, A.A. Mousa, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **2003**, 59, 2577-2584. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [13]. M.R. Almeida, R. Stephani, H.F. Dos Santos, L.F.C.D. Oliveira, *J. Phys. Chem. A*, **2009**, 114, 526-534. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [14]. S. Wang, S. Shen, H. Xu, *Dyes Pigm.*, **2000**, 44, 195-198. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [15]. E. Weglarz-Tomczak, L. Gorecki, *Chemik*, **2012**, 66, 1298-1307 [[Crossref](#)], [[Google Scholar](#)]
- [16]. G.R. Ferreira, L.F.C. de Oliveira, *J. Mol. Struct.*, **2017**, 1146, 50-56. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [17]. K. Hunger, P. Mische, W. Rieper, Azo Dyes, *Ullmann's Encyclopedia of industrial chemistry*. **2011**, 242. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [18]. M.E. Radulescu-Grad, S.G. Muntean, A. Todea, O. Verdes, A. Andelescu, *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)*, **2015**, 60, 37-40. [[Crossref](#)], [[Google Scholar](#)]
- [19]. I. Mansoor, Textile Dyes. Rehbar Publisher Karachi Pakistan, **2008**, 120. [[Google Scholar](#)], [[Publisher](#)]
- [20]. G. Mawla, Different types of dyes with chemical structure, **2012**. [[Google Scholar](#)], [[Publisher](#)]
- [21]. G.A. Soleimani, J.A. Taylor, *Dyes Pigm.*, **2006**, 68, 109-117. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [22]. G. Hussain, N. Abass, S. Glulain, A. Makshoof, A. Saeed, R. Saleem, F. Ali, M. Ain Khan, *J. Appl. Res. Technol.*, **2017**, 15, 346-355. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [23]. K.J. Sakoma, K.A. Bello, M.K. Yakubu, *Open J. Appl. Sci.*, **2012**, 54-59. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [24]. P.O. Nkeoye, Fundamental Principles of Textile Dyeing, Printing and Finishing. Ahmadu Bello University Press, Zaria, Nigeria, **1987**, 91-111. [[Google Scholar](#)], [[Publisher](#)]

- [25]. E.R. Trotman, Dyeing and Chemical Technology of Textile Fibres, Charles Griffin and Company Ltd., England, **1984**, 481. [[Google Scholar](#)], [[Publisher](#)]
- [26]. J. Shore, Colourant and Auxiliaries. Society of Dyers and Colourists, Bradford, **2002**, *1*, 356-440. [[Google Scholar](#)], [[Publisher](#)]
- [27]. A. Marini, A. Munoz-losa, A. Biancardi, B. Mennucci, *J. Phys. Chem. B*, **2010**, *114*, 17128-17135. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [28]. M. Ayaz, F. Ali, G. Shabir, A. Saeed, N. Ali, N. Abbas, G. Hussain, P. Channar, M. Ayaz, *J. Appl. Res. Technol.*, **2019**, *17*, 66-77. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [29]. H. Musa, A. Abdulmumini, M.O. Folashade, B. Usman, H. Abba, *IOSR J. Appl. Chem.*, **2013**, *5*, 11-17 [[Crossref](#)], [[Google Scholar](#)]
- [30]. L.K. El-Gabry, M.M. El-Zawahry, *Res. J. Text. Appar.*, **2008**, *12*, 21-30. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [31]. O.O. Nnorom, P.I. Anyanwu, C.K. Oguzie, S.D. Okonkwo, *Int. J. Text. Sci. Tech.*, **2020**, *6*. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [32]. C.D. Prajapati, E. Smith, F. Kane, *Color. Technol. Soc. Dye. Colour.*, **2018**, *134*, 423-439. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [33]. M.K. Goftar, K. Moradi, N.M. Kor, *Eur. J. Exp. Biol.*, **2014**, *4*, 72-81. [[Crossref](#)], [[Google Scholar](#)]
- [34]. H. Kocaokutgen, E. Erdem, I.E. Gümrükçüoğlu, *J. Soc. Dye. Colour.*, **1998**, *114*, 93-95. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]