



## SYNTHESIS AND CHARACTERIZATION OF Cu AND Fe (1:2) METAL COMPLEXES BASED ON THEIR SUBSTITUTED PYRIDONES ACID DYES AND THEIR APPLICATION ON WOOL FABRICS

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### ARTICLE INFO

### ABSTRACT

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#### Article history:

Received 13 October 2022  
Received in revised form 30 November 2022  
Accepted 25 December 2022  
Available online 30 December 2022

#### Keywords:

4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone  
Pyridone derivatives  
Metallized acid dyes  
Applications and Fastness properties

In this study, the investigation deals with synthesis of acid dyes from 4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone and their pyridone derivatives and their metal complexes (Cu (II) and Fe (II)). The pyridone derivatives include 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-buthyl-2-hydroxy-4-methyl-5-cyano-6-pyridone. The acid dyes were successfully synthesised with good yield ranging from 75-96% and were metallized using Cu (II) and Fe (II) in the ratio 1:2. Metallized acid dyes with Cu (II) and Fe (II) were successfully synthesised with good yield ranging from 82-96%. Characterization of these dyes structure were confirmed by UV, FTIR and GCMS. These acid dyes were applied on wool fabrics to access their dyeing properties. All these acid dyes gave yellow, greenish yellow, dark grey and brown color shades. The washing fastness showed moderate to excellent (4-7), rubbing fastness indicate good to excellent in wet and dry (3-5) and fastness to perspiration showed moderate to very good (3-4) on wool fabrics. The fastness properties of non-metallized acid dyes were less as compared to metal complex acid dyes due to high tinctorial strength and efficient exhaustion of metallized dyes on wool fabrics using pH of 6.

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### Introduction

A dye is a coloured soluble organic compound that grips light intensely in the visible region and can firmly fasten to the fiber by chemical and physical bonding between site of attraction in the dye and group on the

commercial importance a dye should be fast to light, rubbing and water [1].

The colour of a compound is related to its chemical constitution [2]. The relationship between colour and chemical constitution of a substance has been explained by different theories, including: Witt's theory (1976),

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which states that there existed a relationship between colour and chemical constitution of a compound and that, a dye is made up of two parts: chromophore and auxochromes. According to Witt, colour usually appears in an organic compound if it contains certain unsaturated groups. 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 [2-4]. Azo dyes are the main group of azo compounds and the most extensively used colorants in the industry. Numerous derivatives of pyrazole (azo) were the subject of research because of their diversity of applications. The applications of the azo dyes include their use in dyeing fibers, owing to their strong affinity for wool and silk [5], photoelectronics [6], printing systems as well as in analytical and food chemistry. Beside these many azo compounds have been synthesized with an industrial and medical aim [7-10].

Azo dyes are the largest class of synthetic dyes which contribute 60-70% of the total production synthetic dyes being used currently. Extensive spread ability and synthesis of azo dyes is due to their high molar extinction coefficient, high solubility, medium to high fastness, high substantivity, diversity in structures, easy accessibility of raw materials and simple synthetic procedures. Here are several classes of azo dyes for example reactive dyes, metal complex dyes, direct dyes, vat dyes. Amid these different classes of dyes, direct dyes are stress-free to synthesize and apply. Direct dyes are applied on cotton and nylon fibers in neutral or slightly alkaline medium.

## Results and Discussion

### *Synthesis and characterization of ligand pyrazolone acid dyes and their metal complexes*

Synthesis of acid dyes and their iron (Fe, II) and copper (Cu, II) complexes were prepared in five step procedure as shown in Scheme of reaction. [1-(4-sulphophenyl)-3-methyl-2-pyrazolin-5-one] was nitrosated at 0–5 °C using  $NaNO_2$  and HCl. The nitroso compound was filtered to dry and purified. The clarified nitroso derivative [that usually exists in an oxime form (as indicated by its FTIR)] was salted out by common salt. Reduction of oxime was carried at 100–105 °C using zinc and HCl. The oxime and zinc were alternatively added in small portions in boiling HCl solution [8].

The reduction was completed as the solution became colorless. The resultant amine hydrochloride was quenched to –7 °C. This amine hydrochloride was diazotized using an aqueous solution of  $NaCO_3$  (5.38 g dissolved in 2.564 ml of solution) and HCl at –5 to –2 °C to escape the development of Rubazotic acid, which is

automatically formed during this reaction with increasing temperature owing to oxidizing action of nitrous acid, formed in situ. The diazonium salt prepared in this way was coupled with different 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. The synthesized dyes **6a–d** were precipitated on completion of reaction by reducing the pH of solution to 1.0 with HCl. The filtered dyes were dried and purified in ethanol.

Metallization of these dyes was produced by treating their alkaline solution with  $FeSO_4 \cdot 7H_2O$  and  $CuSO_4 \cdot 5H_2O$  at 65–70 °C. It took about 4–5 h to complete the metallization as was obtained by taking the TLC of reaction mixture in 9:1 chloroform and methanol. Dyes (**8a–h**) were precipitated with addition of HCl, filtered and dried in oven at 80 °C. These dyes were again purified from ethanol, dried, weighed and determined the percentage yield. These unmetallized dyes **6a–d** are tridentate ligands which form complexes with iron (Fe, II) and copper (Cu, II) through 1:2 metal and ligand stoichiometric ratio in the reaction scheme above. In case of  $Fe^{2+}$  and  $Cu^{2+}$  complexes lone pairs of electrons are contributed by two oxygen atoms and one nitrogen atom of the diazo linkage, whereas the other three coordination numbers of these metals have been satisfied by three water molecules. The complex formation pattern has been verified by the UV–vis spectrophotometric studies of these dyes **8a–h**. In case of IR spectra of compounds different moieties displayed stretching and bending bands characteristic of the synthesized compounds.

**Table 1.** Physical characteristics of acid dyes based on Pyridone derivatives.

Dye(Molecular Formular)	Molecular Mass (gmol <sup>-1</sup> )	Melting Point (° C)	Yield (%)	Colour of Crystal
<b>6a</b> (C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub> S)	430	342-344	75	Yellow
<b>6b</b> (C <sub>17</sub> H <sub>17</sub> N <sub>6</sub> O <sub>6</sub> S)	445	345-347	95	Yellow
<b>6c</b> (C <sub>19</sub> H <sub>19</sub> N <sub>6</sub> O <sub>6</sub> S)	460	304-306	90	Yellow
<b>6d</b> (C <sub>21</sub> H <sub>23</sub> N <sub>6</sub> O <sub>6</sub> S)	488	310-312	96	Yellow
<b>7e</b> (C <sub>34</sub> H <sub>24</sub> CuN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	919	430-432	93	Deep Brown
<b>7a</b> (C <sub>34</sub> H <sub>24</sub> FeN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	912	336-338	91	Brown
<b>7f</b> (C <sub>36</sub> H <sub>28</sub> CuN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	949	410-412	92	Black grey
<b>7b</b> (C <sub>36</sub> H <sub>28</sub> FeN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	942	411-412	91	Black grey
<b>7g</b> (C <sub>38</sub> H <sub>32</sub> CuN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	979	355-357	90	Deep brown
<b>7c</b> (C <sub>38</sub> H <sub>32</sub> FeN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	972	411-414	80	Deep brown
<b>7h</b> (C <sub>42</sub> H <sub>36</sub> CuN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	1035	436-438	92	Green
<b>7d</b> (C <sub>42</sub> H <sub>36</sub> FeN <sub>12</sub> O <sub>12</sub> S <sub>2</sub> )	1028	436-437	91	Yellow

#### Physical characteristic of the synthesized dyes

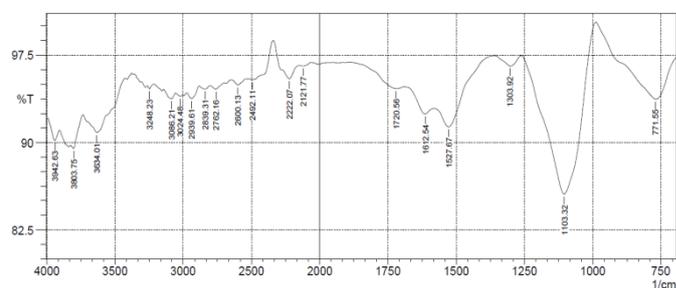
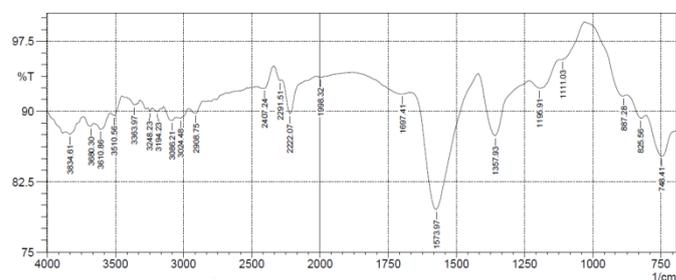
The Physical characteristics of the dyes are shown in Table above. Each of the different dyes synthesized possessed unique physical characteristics. They have well-defined melting points (342-438°C), yield point and molecular mass characteristics of pure compounds.

#### UV Visible spectral of the dyes

From the detailed UV-Vis study of dyes it was gathered that metal complexes of ligand dyes bearing electron with drawing groups showed hypsochromic shift and those having electron donating groups showed bathochromic shift in absorbance which is in accordance with the well-established UV-visible absorption pattern of compounds [8].

Change in colour of dyes after metal complex formation depends upon electron accepting or donating ability of d-orbitals either it is large or small. This largest shift in iron (II) complex is attributed to three unpaired electrons in the 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 colours after complex formation [11].

The infrared spectra of the synthesized acid dyes and their metal complexes exhibited absorption peaks due to O - H str, C-H str. Aliphatic, C-H<sub>3</sub> 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 depicted from the FTIR spectra (Figure 1).

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

**Table 2.** The wavelength of maximum absorption and Molar coefficient of the dyes.

Dye	E <sub>max</sub> in Ethanol 10 <sup>4</sup> Lmol <sup>-1</sup> cm <sup>-1</sup>	Ethanol λ <sub>max</sub> (nm) a	Ethano+ HCL λ <sub>max</sub> (nm) b	Dist. H <sub>2</sub> O λ <sub>max</sub> (nm)	Change in λ <sub>max</sub> (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
7e	7.92	413	412	434	-1
7a	5.75	434	593	433	159
7f	5.47	413	412	428	-1
7b	6.13	422	433	422	11
7g	4.68	421	434	431	3
7c	4.88	437	431	433	-6
7h	5.97	450	425	429	-25
7d	5.98	433	434	421	1

The mass spectrum of dye 6a gave mass-to-charge ratio (m/z) of 77, 148, 158, 254, 282, and parent 429.1 representing molecular ion (m) and the corresponding positive charge fragment of C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>S<sup>+</sup>, C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>17</sub>H<sub>14</sub>N<sub>6</sub>O<sub>6</sub>S<sup>+</sup>, are shown respectively in Figure 3. Hence, the theoretical value is 430 when compared to the mass spectrum value of 429.1 due to isotopes.

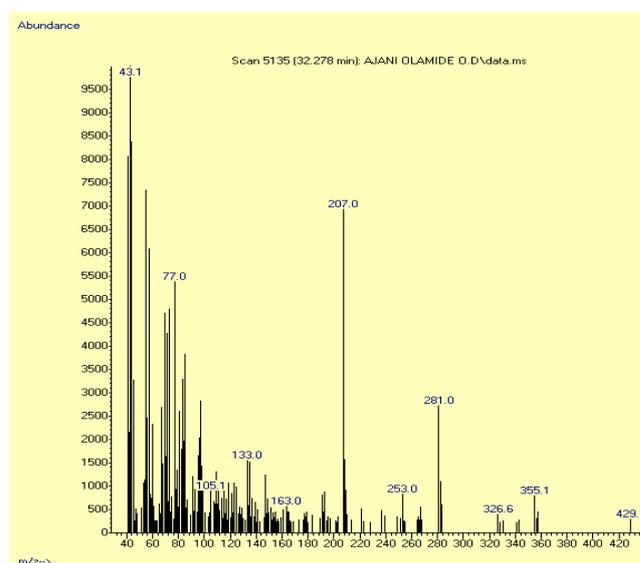
The mass spectrum of dye 6d gave mass-to-charge ratio (m/z) of 77, 158, 206, 254, 282, and parent 489 representing molecular ion (m) and the corresponding positive charge fragment of C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>S<sup>+</sup>, C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>21</sub>H<sub>23</sub>N<sub>6</sub>O<sub>6</sub>S<sup>+</sup>, are shown respectively in Fig 4 below.

#### 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.

#### Percentage (%) exhaustion of synthesized dyes

The percentage (%) dye exhaustion of the synthesized dyes on wool is shown in the figure (5) below:



**Figure 3.** GCMS of synthesized BAP dye (6d) with pyridone coupling component.

#### The effect of pH on the dye exhaustion

The effect of pH on the dye exhaustion (%) is carried out on nylon 6.6 fabrics shown in the figure (7) below:

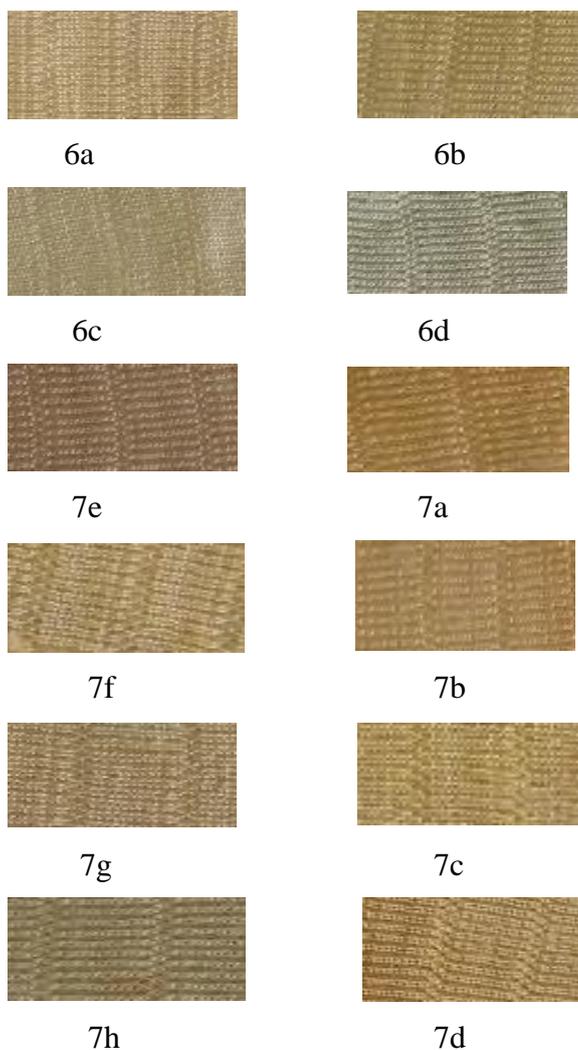


Figure 4. shade of dyes 6a-6d; 7a-d; 7e-h on wool.



Figure 6. Percentage (%) Exhaustion of synthesized dyes on Wool.

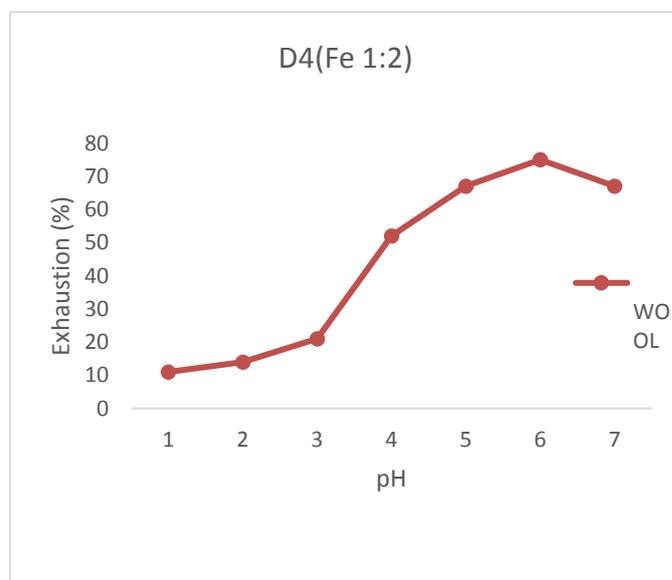


Figure 7. Effect of pH on dye Exhaustion, showed wool have pH at 6.

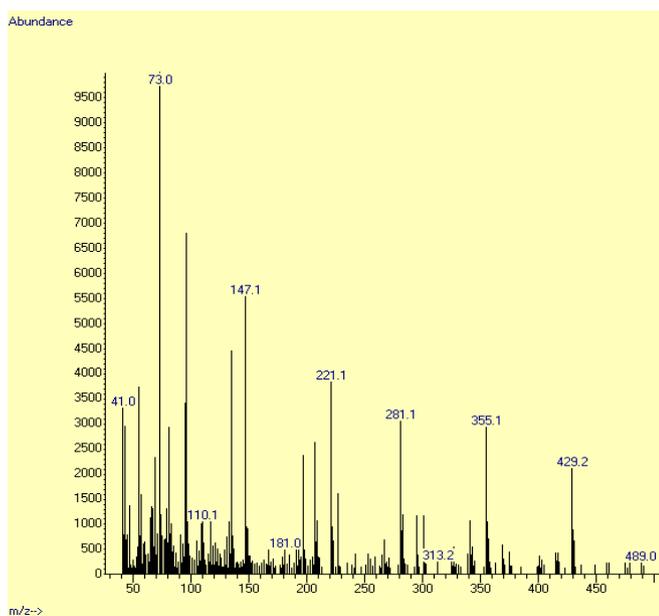


Figure 4. GCMS of synthesize BAP dye (6d) with pyridone coupling component.

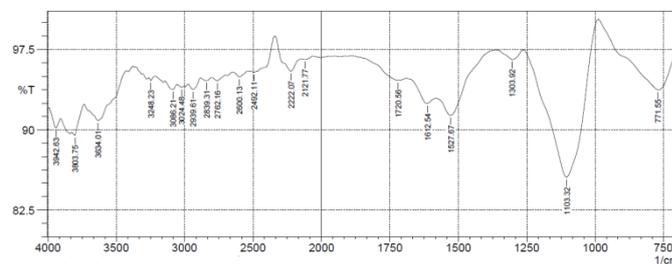


Figure A. FTIR of Dye 7a (Cu 1:2).

**Table 3.** Light and Washing Fastness Properties of the synthesized dyes on Wool

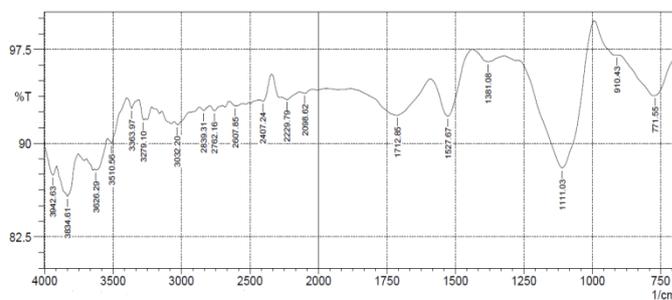
Dye code	Fastness	
	Light Wool	Washing Wool
6a	5	4
6b	6	3
6c	5	4
6d	6	4
7e	6	3
7a	6	4
7f	5	4
7b	6	4
7g	6	3
7c	6	4
7h	5	4
7d	4	4

**Table 4.** Fastness to perspiration properties of the synthesized dyes on wool.

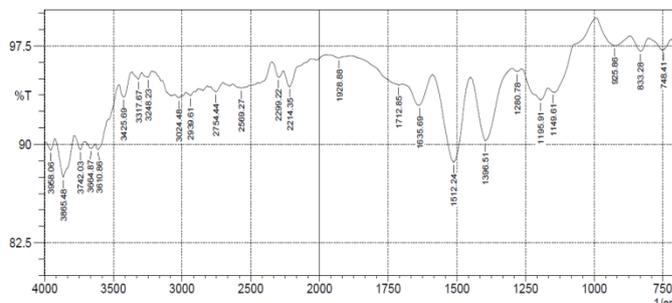
Dye code	Fastness to perspiration	
	Acid Wool	Alkaline Wool
6a	4	4
6b	4	4
6c	4	4
6d	4	4
7e	3	4
7a	3	4
7f	4	4
7b	3	4
7g	3	4
7c	3	4
7h	3	4
7d	4-5	4-5

**Table 5.** Rubbing fastness properties of the synthesized dyes on wool.

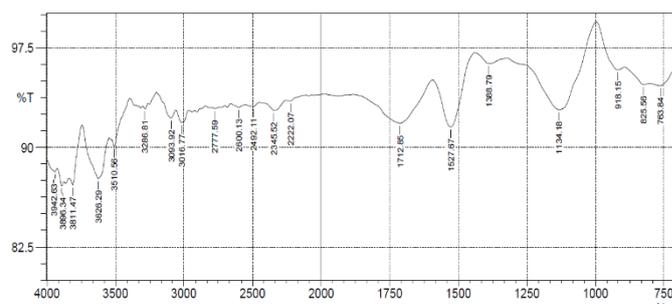
Dye code	Rubbing Fastness	
	Dry Wool	Wet Wool
6a	4-5	4-5
6b	4-5	4-5
6c	4-5	4-5
6d	4-5	4-5
7e	4-5	4-5
7a	4-5	3-4
7f	4-5	3-4
7b	4-5	4-5
7g	4-5	4-5
7c	4-5	3-4
7h	4-5	4-5
7d	4-5	4-5



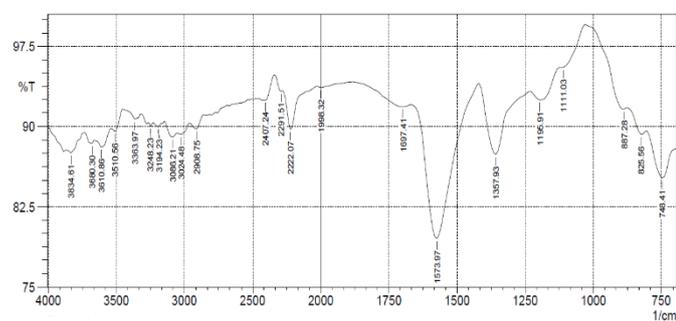
**Figure A.** FTIR of Dye 7f (Fe 1:2).



**Figure A.** FTIR of Dye 7b (Fe 1:2).



**Figure A.** FTIR of Dye 7g (Fe 1:2).



**Figure A.** FTIR of Dye 7e (Fe 1:2).

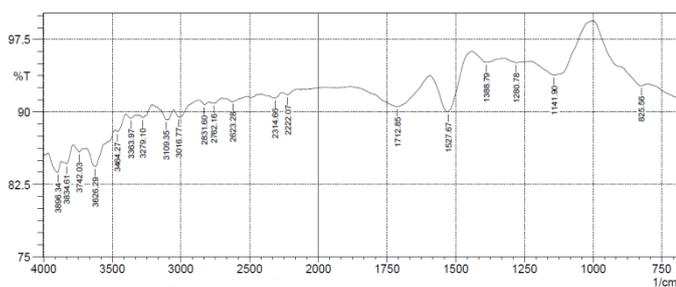


Figure A. FTIR of Dye 7c (Fe 1:2).

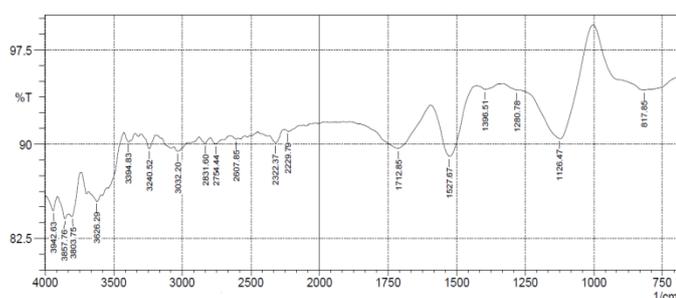


Figure A. FTIR of Dye 7h (Fe 1:2).

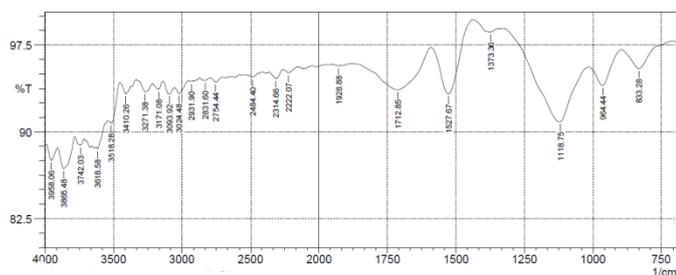


Figure A. FTIR of Dye 7d (Fe 1:2).

## Experimental

The methods adopted for this research work were of scientific approach, weighing and measuring all chemicals with adequate precautions. The results were recorded as quickly as possible to avoid human error.

### Synthesis of acid 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. Also, metallization was done using Cu (II) and Fe (II).

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

1-(p-sulfophenyl)-3-methyl-5-pyrazolone (5.08 g, 0.1 mol) was suspended in H<sub>2</sub>O (50 ml). Hydrochloric acid

(9 ml) was added to this well stirred suspension using magnetic stirrer. The reaction mixture was cooled to 0–5 °C in an ice bath. A solution of NaNO<sub>2</sub> (1.38 g, 0.1 mol) in H<sub>2</sub>O (5 ml) previously cooled to 0 °C, was then added over a period of 35 min with stirring. The stirring was continued for 1 hr maintaining the same temperature, with a positive test for nitrous acid. Later on the excess of nitrous acid was destroyed with required amount of sulphamic acid. The nitroso (oxime) was filtered after salting out. Then oxime was reduced by stirring in 40 ml water containing 17 ml HCl and 4.6 g zinc metal at boil for 4h. On completion of reaction, pH of the reaction mixture was raised to 9 with 6N NaOH, and precipitated the 1-(p-methylphenyl)-3-methyl-4-amino pyrazolones [8].

### Diazotization and coupling with pyridine derivative

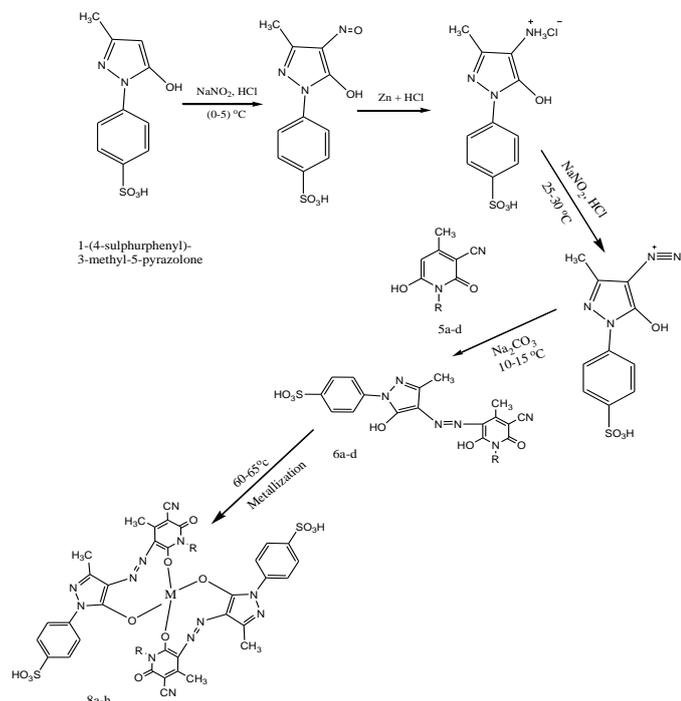
To the well-stirred ice jacketed aqueous solution (0.538 g) of 1-(p-sulphophenyl)-3-methyl-4-amino pyrazolone (at 0–5 °C) was added conc. HCl (0.7 ml) and sodium nitrite solution (0.7g in 2 ml H<sub>2</sub>O). The reaction mixture was intensely stirred for 1h using magnetic stirrer at the above mentioned temperature to produce the diazonium salt of 1-(p-sulphophenyl)-3-methyl-4-amino pyrazolone. The diazonium compound formed in this way was coupled to various coupler mentioned previously to synthesize our dyes. Thus 2.69g (0.01 mol) 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone (4a) was dissolved in 12.82 ml water containing 2.69g NaCO<sub>3</sub> and coupled with prepared diazo. The reaction mixture was given 2–3h to complete the coupling at 30–35 °C. The dye was cooled to room temperature. Its pH was reduced to 4.5 by HCl and filtered. The cake was dried in oven at 50 °C till constant weight. By adopting the same procedure other dyes 6b–d were prepared from couplers 5b–d as shown in the reaction scheme below.

### Metallization of acid dyes

For the synthesis of metal complexes (iron complex), 25 ml (0.005 mol) of dye 6a was reduced to a pH of 6.5 with HCl. Then it was heated to 65–70 °C and to it 5 ml (0.005 mol Fe<sup>2+</sup>) solution of ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was added drop wise. Mixing and heating at this temperature was continued for further 4–5 h till the metallization was completed. The dye was cooled to room temperature; its pH was reduced to 1.0 with conc. HCl. Then it was salted out with sodium chloride, filtered and dried in oven at 50 °C till constant weight.

Similarly, copper (II) complexes of dye 6a were prepared by treating dye with CuSO<sub>4</sub>·5H<sub>2</sub>O at 70 °C with metal to ligand mole ratio 1:2. In this way complexes 7a–h were synthesized from respective dye ligands (see supplementary information). Also the two metal complexes CU(II) and Fe(II) complexes of dye 6a were

prepared by treating with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  at 65-70 °C with metal to ligand mole ratio 1:2. In this way complexes 8a-h were synthesized from respective dye ligands (see supplementary information).



**Scheme of Reaction:** Synthesis of ligand acid dyes 7a-d and their Fe (II); Cu (II) complexes (8e-h).

5a-6a R= H	8a R= H , M= Fe (II) (1:2)	8e
R= H , M= Cu (II) (1:2)		
5b-6b R= CH <sub>3</sub>	8b R= CH <sub>3</sub> , M= Fe (II) (1:2)	8f
R= CH <sub>3</sub> , M= Cu (II) (1:2)		
5c-6c R= C <sub>2</sub> H <sub>5</sub>	8c R= C <sub>2</sub> H <sub>5</sub> , M= Fe (II) (1:2)	8g
R= C <sub>2</sub> H <sub>5</sub> , M= Cu (II) (1:2)		
5d-6d R= C <sub>4</sub> H <sub>7</sub>	8d R= C <sub>4</sub> H <sub>7</sub> , M= Fe (II) (1:2)	8h
R= C <sub>4</sub> H <sub>7</sub> , M= Cu (II) (1:2)		

### Dyeing method

### Dyeing of wool

The dye bath was prepared using a liquor ratio of 50:1 and 2% shade on the weight of fabric. The dye bath containing acetic acid of 2ml and pH of the dye bath was adjusted to 6.

For dyeing of wool, 1g of fabric was wetted in water for 5 minutes and excess water squeeze out. The wetted fabric was then introduced into the dye solution on a regulatory steam bath with dyeing temperature at 80-90°C initially and raised gradually to boil over 60 minute while agitating the sample. Dyeing was carried out at boil for 1 hr. After, dyeing was completed, the fabric was removed, thoroughly rinsed with cold water and dried at room temperature.

### Conclusion

The hitch of dyes with unsatisfactory tinctorial strength and fastness properties in textile dyeing have been resolved with the new acid dyes that were synthesized starting from p-sulphophenyl-3-methyl-5-pyrazolone 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 dyes. These non-metal complex dyes undergo metallization with Fe (II) and Cu (II) complex ion resulting to the metal complex dyes. The synthesized acid dyes were applied on nylon 6.6 fabrics. All the dyes gave yellow, greenish yellow, dark grey and brown coloured shades. The synthesized dyes have high tinctorial strength, and good colour fastness to washing, light, rubbing and perspiration, indicating the existence of strong bonds (ionic bonds) between the dye and fabrics. Exhaustion of the dyes are very good which indicates that the dyes have good affinity for the fabrics.

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