



“Ecofriendly” synthesis, characterization and dyeing of azo based acid dyes on nylon fabrics

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ABSTRACT

A novel series of transition metal complex azo dyes of Cu, Ni and Co have been yielded from 5-Bromo-2[[5-hydroxy-3-methyl]-1-[[2'-methyl-5'-sulphophenyl]-1H-pyrazol-4yl]diazanyl benzoic acid and aqueous solution of metals derived from diazonium salt of 2-Amino-5-Bromo benzoic acid. The molecular formulae of the synthesized compounds were assigned on the basis of elemental analysis while the structures were proposed on the basis of FT IR and ¹H NMR. The dyeing assessment of the synthesized dyes was evaluated on nylon fabrics. The percentage dye bath exhaustion on the fibers has been found to be reasonably good and acceptable. Further, the light fastness of the dyed nylon fibers was moderate to very good and washing fastness was good to excellent.

Keywords: azo, transition metals, dyeing, nylon, fastness properties.

INTRODUCTION

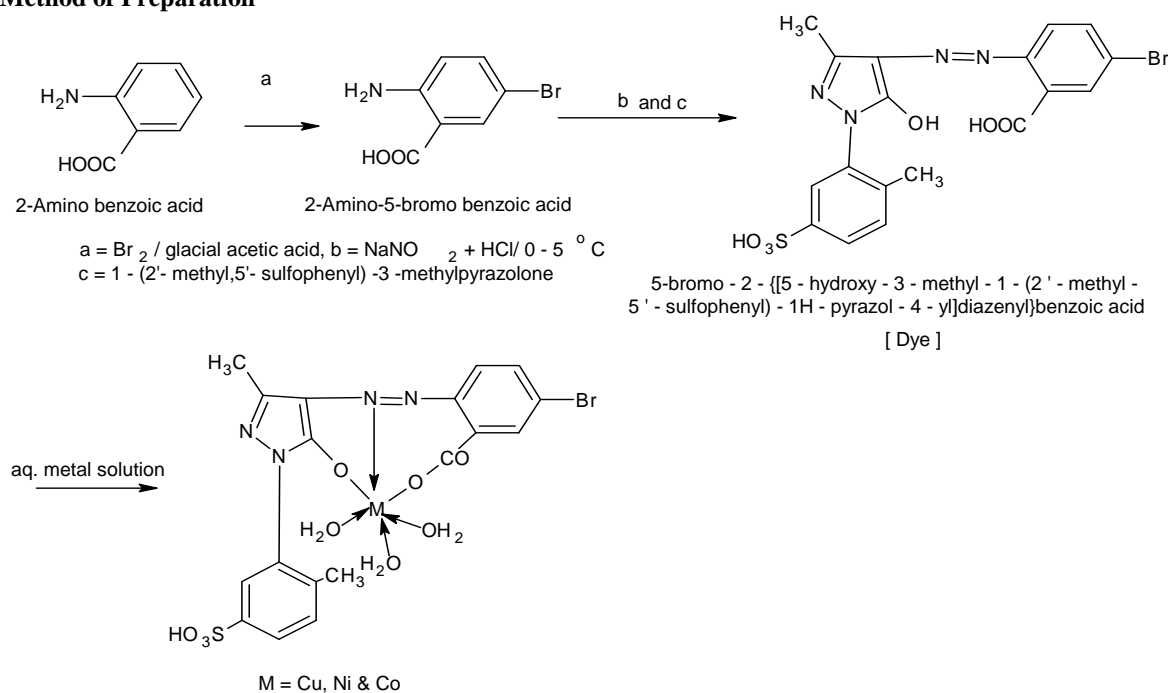
Traditionally, acid azo dyes are the most important class of commercial dyes, occupying more than half of the dye industries, which contain various intermediates[1,2]. Out of the different classes of dyes, azo dyes constitute the largest group of colorant used in the industry [3,4,5]. They are usually strongly colored compounds which can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their color, azo compounds are of tremendous importance as dyes and also as pigments for a long time[6]. They have wide application in analytical chemistry, metallurgy, the textile industry, optical data storage, photo switching and nonlinear optical materials [7–11]. Thus, the synthesis of ligands incorporating –N=N– group is an important field of research. Notable examples of these ligands are arylazobenzene [14], arylazooxime[15], arylazophenol[16], arylazopyridine[12,13,17], arylazoimidazole[18], arylazopyrimidine [19], and arylazoaniline [20].

The coordination chemistry of transition metals with azo ligands is being studied due to the observation of several interesting properties. In our present investigation, a series of novel acid azo dyes were prepared by coupling aromatic diazonium salts with transition metals and characterized the dyeing assessment of such dyes on nylon textile fibers reveals that excellent results were achieved. During the dyeing assessment it was observed that the produced dye have powerful fixation properties. The dyes fixed on the fiber with almost negligible unused dye. Most of the dyes have high fixation on textile at less percentage of exhaustion. While using these dyes commercially it may affect the environmental saving by less percentage of dye effluents from textiles. This study was also conducted on wool and silk fabrics [21,22].

EXPERIMENTAL SECTION

All the employed reagents were of analytical grade and the solvents were purified by standard methods. All melting points reported were taken in open capillaries and are uncorrected. The purity of the compounds was checked routinely by TLC(0.5mm) thickness using silica gel-G coated Al-plates (Merck) and spots were visualized by exposing the dry plates in iodine vapors. Infrared spectra ($4000\text{-}400\text{cm}^{-1}$) taken on KBr disc using a Perkin-Elmer Spectrum BX series IR spectrophotometer. ^1H NMR spectra were recorded on Avance Bruker 800 MHz NMR Spectrometer. Elemental analysis was performed on Carlo Erba 1108 analyzer. Fastness to light and washing was assessed in the accordance with BS: 1006-1978 is 765-1979 respectively whereas rubbing fastness was carried out with a Crock meter (Atlas) in accordance with AATCC-1961.

Method of Preparation

**Preparation of 2-Amino-5-bromo benzoic acid:**

2-Amino benzoic acid(20g) was dissolved in glacial acetic acid(250 ml) was cooled below 16°C . Bromine(9.5 ml) was added and the mixture was stirred for 2-3 hours vigorously. The precipitates obtained were boiled with water(500 ml) containing concentrated hydrochloric acid (25 ml).The hot boiling solution was filtered rapidly and the filtrate obtained was cooled in ice-bath. The filtrates upon cooling yielded abundant precipitates of the 2-Amino-5-bromobenzoic acid (M.P 219°C) and insoluble residue consisted of the 2-Amino-3,5-dibromo benzoic acid(M.P. 235°C)

Preparation of diazonium salt of 2-Amino-5-Bromo benzoic acid: (2b)

2-Amino-5-bromobenzoic acid (0.01moles) was suspended in water (50 ml), concentrated hydrochloric acid (3.0 ml, 0.025mole) was added drop-wise to the well stirred suspension and the resultant clear solution was cooled to $0\text{-}5^\circ\text{C}$ in ice-bath. A solution of sodium nitrite(0.012moles) in water (10 ml) previously cooled to 0°C was then added and the reaction mixture was stirred for an hour and the diazo was used for the subsequent coupling.

Preparation of 5-Bromo-2[[5-hydroxy-3-methyl]-1-[[2'-methyl-5'-sulfophenyl]-1H-pyrazol-4yl]diazanyl benzoic acid :(Dye)

1-(2'-Methyl,5'-sulfophenyl)-3-methylpyrazolone(0.01mole) was dissolved in Na_2CO_3 solution(10% W/V and cooled to $0\text{-}5^\circ\text{C}$ in an ice-bath. A well stirred diazonium solution of 2-amino-5-Bromo benzoic acid was added and stirring was continued for 3 hours at $0\text{-}5^\circ\text{C}$ and pH was adjusted to 7 by adding Na_2CO_3 (10% W/V). NaCl solution

(10% W/V) was added after completion of reaction with stirring to precipitate out the solid material. It was then filtered and crystallized from DMSO to get orange yellow crystals. Yield 80%, M.P above 300°C.

Preparation of metal complexes : TP-1(Ni-Dye), TP-2(Cu-Dye) and TP-3(Co-Dye)

5-bromo-2{[5-hydroxy-3-methyl]-1-[(2'-methyl-5'-sulphophenyl)-1H-pyrazol-4-yl]diazonyl}benzoic acid (0.01mole) dissolved in di-oxane slowly added to the hot aqueous solution of metal chloride(0.01mole) Ni(II), Cu(II) and Co(II) with constant stirring and a small amount of sodium acetate (0.5g) added to it. Then the whole mixture was set for an hour. The solid metal complexes were precipitated out and then crystallized with DMF. Crystals of Nickel(II), Copper(II) and Cobalt(II) complexes were obtained with DMF.

The procedure through which nylon fabrics was treated is divided into four major sections

An application of acid dyes on nylon fabrics

Exhaustion of dye-bath

Fixation study of the dyed nylon fabrics

Study of light and washing fastness

An application of acid dyes on nylon fabrics :

Dyeing with acid dye is carried out by following the procedure given below[20,21] :

Pre-treatment of the fabric :

Knitted nylon fabric (2.5 gm) was scoured in a solution containing 2g/L soap solution, ammonia (0.1 mL) and water (100 mL). It was then boiled for 15 minutes. The fabric was removed from the bath and rinsed several times with water. It was then rinsed, dried and conditioned for two days in atmospheric condition and subsequently used for dyeing.

Adjustment of pH of fabrics to a required value :

In order to study of dyeing at a certain pH, it is necessary to adjust pH of the suspended fabrics and solution forming dye-bath to a required value. In order to obtain evenness of pH throughout the material before it enters the dye liquor. A weighted amount of previously treated nylon fabrics was heated for 5 minutes at 95-100°C in a solution which was adjusted to pH 3.0 by adding with acetic acid (10% w/v) solution. The nylon fabrics were removed and squeezed as far as possible to make it free from adhering mother liquor.

Dyeing procedure :

Dye solution (10 ml, 0.4% w/v) was taken in a dye-bath. Glauber's salt solution (7 ml., 20% w/v) was added to it. The pH of the dye-bath was adjusted to 3.0 by adding acetic acid solution (3.5 ml., 10% w/v) solution. The total volume of the dye-bath was adjusted to 80 ml by adding required amount of water. The nylon fabric previously adjusted to pH 3.0 was introduced into the dye-bath with stirring. The content of the dye-bath was stirred for 30 minutes at room temperature. The temperature was then gradually raised to 95°C over period of 30 minutes and maintained for 20 minutes. The dye-bath was kept rotating during the process of dyeing. The fabric was washed with cold water and the combined solution of dye liquor and washings was then further diluted to 250 ml with water. 5 ml of this solution was further diluted to 250 ml with water and the absorbance of this solution was measured. The above pattern was further rinsed, washed and dried and a part of it was mounted on shade cards.

Exhaustion of dye-bath :

The combined solutions of the dye liquor and the washings were diluted to 250 ml with water. 5 ml of this solution was further diluted to 25 ml with water. The percentage dye-bath exhaustion was calculated by measuring the absorbance of the above solution and reading the corresponding concentration on the calibration curve.

The results of percentage exhaustion of dye-bath are shown in Table-1 and 3.

Table-1: Calibration data for Exhaustion study of Acid Dyes TP-1 toTP-3						
Substrate for dyeing: Nylon (2.0 gm), Medium of spectral study : Aqueous						
Dye Code No.	Wave length λ_{max} nm	Absorbance of the dye solutions at specified wavelength conc. $\times 10^{-3}$ mg.m ⁻¹				Slope of linear plot K*
		4.0 Ab.	8.0 Ab.	12.0 Ab.	16.0 Ab.	
TP-1	526	0.100	0.200	0.300	0.400	25.00
TP-2	552	0.090	0.180	0.270	0.360	22.50
TP-3	524	0.070	0.140	0.210	0.280	17.50

Fixation study of the dyed Nylon fabrics :

This involves two steps : construction of calibration curve and estimation of dye which is fixed on the fabric by extraction method using boiling acidic solution of pyridine containing pyridine (10% w/v), 90% formic acid (20% w/v) and water (to 100% vol) instead of water. The data is presented in Table-2 and 3.

Dye Code No.	Wave length λ_{\max} nm	Absorbance of the dye solutions at specified wavelength conc. x 10^3 mg.m ⁻¹				Slope of linear plot K*
		4.0 Ab.	8.0 Ab.	12.0 Ab.	16.0 Ab.	
TP-1	526	0.150	0.300	0.450	0.600	25.00
TP-2	552	0.130	0.270	0.390	0.520	22.50
TP-3	524	0.110	0.220	0.330	0.450	17.50

Estimation of fixation of dye :

Dyed nylon fabric (0.1 gm) was place in corning tube and acidic solution of pyridine (10 mL) till the dye was completely extracted from the fabric. The combined extract was diluted to 50 mL with acidic solution of pyridine. The percentage fixation of the dye was then calculated by measuring the absorbance of this solution and reading the corresponding concentration on the calibration curve. A solution of undyed nylon fabric in acidic solution of pyridine was used as reference solution in colorimetric estimation.

Dye Code No.	Amount of dye remained in dye bath (X mg)	Amount of exhausted from dye bath (40-X) = Y mg	% Exhaustion Y mg/40mg x 100	Amount of dye in 0.1 gm of dyeing a mg.	Amount of dye in 2.0 gm of dyeing (total weight 20a=Z mg)	Fixation= (Z mg/Y mg) x 100%
TP-1	8.87	31.13	77.83	1.31	26.2	84.16
TP-2	5.48	34.52	86.30	1.36	27.2	78.79
TP-3	7.38	32.62	81.55	1.33	26.6	81.55

Color yield on dyed Nylon fabrics :

Measurement of color yield was used as a known technique to ascertain the commercial viability of the prepared dyes for dyeing synthetic fibre and their blends. Further, results obtained might clarify the mode of interaction between the prepared dyes and test fibres. Farag et al¹ had described the measurement of color yield over the fabrics. Color yield was formulated as,

$$\text{Color yield} = Z/A \times 10,$$

Where, Z represents the amount of dye fixed on the fibres and A is the initial amount of dye applied on the fabrics. The measured absorbance at λ_{\max} was used to determine the amount of dye present in the dissolved form in the solvent. The results of the colour yield study of dyes are presented in Table-4

Study of light and washing fastness :

Study of light and wash fastness properties of dyed nylon fabrics

Study of light fastness

The light fastness of a dyed pattern is one of the most important properties desired of a dye. The dye textiles are often exposed to light and here it is essential that the color should not fade on exposure to light. So the study of light fastness of dyes becomes essential.

To study light fastness property of a dyed fabric automatic device known as fadeometer are available. The light fastness study can also be carried out using sunlight microscale MBTF, microscale MB/U source etc.

Park and Smith had examined a number of sources with particular reference to the testing of materials with high light fastness. The authors have indicated several light sources that are suitable for carrying out fastness test on textiles. They have also compared the results of different light sources and their have good correlation.

To study the light fastness property of dyed patterns; microscale light fastness tester was used with the straight mercury vapor lamp (MB/U 400w.). This gives satisfactory results in light fastness evaluation and is especially useful, in that the time required for fading patterns of high fastness is considerably less than with other commonly used fading lamps.

The dyed fabrics were exposed to light along with the standard dye fabrics of specific rating. Such standard samples are blue wool standards developed and produced in Europe and are identified by the numerical designation 1-8. Higher the rating better, is the light fastness. The light fastness study was carried out using Microscale light fastness tester having MB/U mercury lamp. The dyed fabrics along with eight standard samples were routed on test holder. Part of the dyed fabric is exposed to light and part of it is covered. After definite intervals of time, the exposed and unexposed portions of test fabrics were examined and compared with the standard fabrics. Suppose at a given time the test fabric has not faded and the standard pattern rated at 7 has not faded then the light fastness is said to be excellent. Now at the next consecutive inspection if the test pattern has faded but the standard pattern of rating 3 has not faded then the test fabric, has the fair light fastness.

Following the above procedure the light fastness properties of dyes TP-1(Cu-Dye), TP-2 (Ni-Dye) and TP-3(Co-Dye) was evaluated and assessed. The results are tabulated in Table-4.

Study of wash fastness :

The wash fastness of the dyed fabrics is another important property desired off. The dyed textile materials are very often washed with soap and detergents and become necessary that the color should not fade on washing. Therefore to study the wash fastness, five test methods are developed by Indian Standards. The results of wash fastness study of dye TP-1, TP-2 and TP-3 on nylon are presented in Table-4.

(a) **Shade :** Visual observation of the shade cards TP-1, TP-2 and TP-3 reveals the excellent range of shades over the nylon fabrics greenish yellow, pale yellow and yellow shades were obtained.

(b) **Fastness properties :** The examination of data presented in Table-4 reveals following metal complex acid dyes show very good light fastness. The wash fastness was appeared to be excellent fastness for each dyes. The results of light and wash-fastness properties on silk fabrics are presented in Table-4.

Table-4 :Shade, colour yield and fastness properties of Acid dyes on Nylon fabrics						
Dye Code No.	Compound	Shade on Wool	λ_{max} nm	Color yield = (Zmg / 40mg) x100	Light	Wash
TP-1	Cu-Dye	Greenish yellow	526	66.5	4	4
TP-2	Ni-Dye	Deep yellow	552	67.5	6	3-4
TP-3	Co-Dye	Yellow	524	65.0	6	4

RESULTS AND DISCUSSION

Dye

¹H NMR (DMSO, 400 MHz) δ 2.29 (s,3H, Ar-CH₃), 2.33 (s,3H,Ar-CH₃),14.66(s, 1H,Ar-COOH), 8.13 (s, 1H,Ar-OH), 14.2(s, 1H, Ar-SO₃H), 7.27-7.98 (m, 6H, Ar-H) ; IR (KBr, cm⁻¹) alkane 1217.12 (C-H) str , aromatic 3084.85 (C-H)str., 1449.81(C=C)str., 3502 (C-OH)str., Pyrazole 1529.60 (C=N)str., 1045.45 (C-N)str., Carboxylic 1320.10 (C-COOH), 2750.81 (-SO₃H), Halide 709.83(-C-Br); Yield: 82%

TP-1 :

¹H NMR (DMSO, 400 MHz) δ 2.33 (s,3H, Ar-CH₃), 2.54 (s,3H,Ar-CH₃), 14.67 (s, 1H, Ar-SO₃H), 7.31-8.13 (m, 5H, Ar-H) ; IR (KBr, cm⁻¹) alkane 1255.32 (C-H) str , aromatic 3069.89 (C-H)str., 1474.28 (C=C)str., 3233.10 (C-OH)str., Pyrazole 1511.43 (C=N)str., 1359.33 (C-N)str., Carboxylic 1368.92 (M-COOH), 592.27 (M-O), 468.91 (M-N), Sulphonic 2777.87 (-SO₃H), Halide 668.37(-C-Br); Yield: 80%

TP-2 :

¹H NMR (DMSO, 400 MHz) δ 2.34 (s,3H, Ar-CH₃), 2.62 (s,3H,Ar-CH₃), 14.77 (s, 1H, Ar-SO₃H), 7.28-8.20 (m, 5H, Ar-H) ; IR (KBr, cm⁻¹) alkane 1245.92 (C-H) str , aromatic 3036.26 (C-H)str., 1464.48 (C=C)str., 3289.12 (C-OH)str., Pyrazole 1499.54 (C=N)str., 1377.98 (C-N)str., Carboxylic 1397.45 (M-COOH), 566.23 (M-O), 455.90 (M-N), Sulphonic 2763.63 (-SO₃H), Halide 675.22(-C-Br); Yield: 86%

TP-3 :

H NMR (DMSO, 400 MHz) δ 2.32 (s, 3H, Ar-CH₃), 2.59 (s, 3H, Ar-CH₃), 14.83 (s, 1H, Ar-SO₃H), 7.39-8.23 (m, 5H, Ar-H) ; IR (KBr, cm⁻¹) alkane 1264.83 (C-H) str , aromatic 3025.83 (C-H)str., 1423.14(C=C)str., 3258.72 (C-OH)str., Pyrazole 1434.80 (C=N)str., 1349.86 (C-N)str., Carboxylic 1345.6 1(M-COOH), 547.32 (M-O), 445.88 (M-N), Sulphonic 2895.54 (-SO₃H), Halide 685.45(-C-Br); Yield: 81%

CONCLUSION

In conclusion, acid dye metal complexes TP-1, TP-2 and TP-3 were synthesized. The exhaustion and fixation of these dyes are very good; this indicates that the dyes have good affinity and solubility with the fabrics. The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes on the fabrics. The washing fastness appeared to be excellent for each dyes thus proved to be eco-friendly. The dyes gave different shades of greenish yellow, deep yellow and yellow having very good fastness properties. These dyes if used commercially it may be harmless to the environment as less percentage of dye effluents from textiles.

Acknowledgement

I would like to be thankful Head of Department of Chemistry for providing the laboratory facilities for my research work. I gratefully acknowledge the most willing help, co-operation and providing facilities for spectral studies by SAIF, Punjab University Chandigarh. I am thankful to all those who have given me direct or indirect support during my research work

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