

## SYNTHESIS AND APPLICATION OF AZO-NAPHTHOL DYES ON WOOL, SILK AND NYLON FABRICS

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### Abstract

Two novel azo-dyes were synthesized by coupling of diazo solutions of p-anisidine and 2-nitro aniline with sodium-2-naphthoate followed by acidification at ice cold condition. The resultant dyes namely 4-methoxybenzeneazo-2'-naphthol and 2-nitrobenzeneazo-2'-naphthol were characterized by elemental analysis as well as IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectral studies. The UV-VIS spectral data has also been discussed in terms of structural property relationship. The dyeing assessment of the synthesized dyes was evaluated on wool, silk, and nylon fabrics. The results showed better hue with good colorfastness to washing, rubbing, and light. The dyes were also evaluated for *in vitro* antibacterial activity against different strains of gram-negative and gram-positive bacteria. The results of the antibacterial properties of these dyes revealed that both the dyes were resistant to aerobic bacterial degradation but dye 2 showed more antibacterial effect than dye 1.

**Keywords:** Azo-dyes, wool, silk, nylon, dyeing.

### Introduction

Out of different classes of dyes, azo dyes constitute the largest group of colorants used in industry [1]. Azo dyes do not occur in nature and are produced only through chemical synthesis [2]. The emergence of diverse classes of synthetic dyes including azo-dye occurred due to constant effort to find specific dye or a particular class of dye for application on diverse materials of industrial importance mainly textile fibres, aluminium sheet, leather, electro optical devices, ink –jet printers etc. [3]. A vast amount of work have been reported on o,o'-dihydroxyazo aminothiazole based dyes in the last decade [4-7]. But so far no work has been done on the synthesis of hydroxyazo naphthalene acid azo dyes suitable for protein and amide fibres.

The present study focused on the synthesis and characterization of 4-methoxybenzeneazo-2'-naphthol and 2-nitrobenzeneazo-2'-naphthol dyes and investigated their application on wool, silk and nylon fabrics.

### Experimental

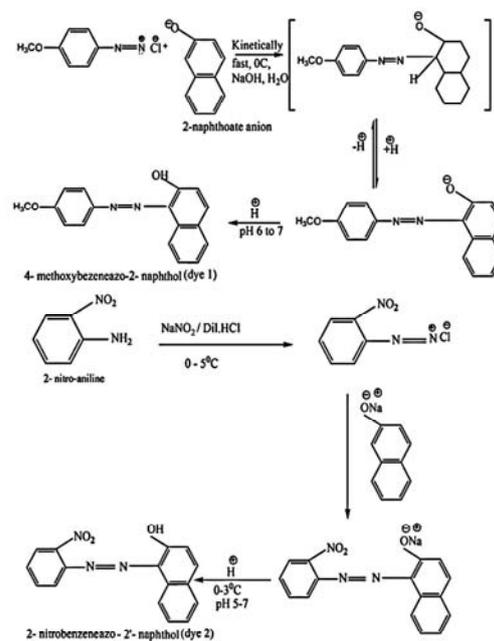
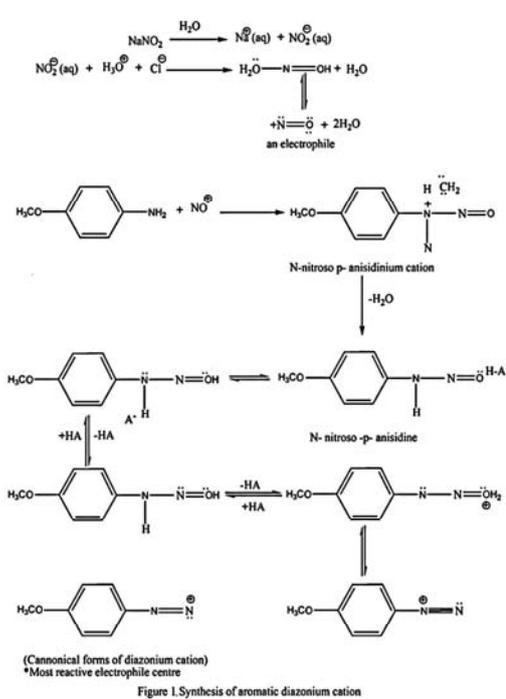
#### Materials

For dyeing experiments degummed and bleached silk fabric (22<sup>d</sup>×34<sup>d</sup> count, 45×38 threads/cm wrap × fill and 56.48 g/m<sup>2</sup> plain weave), bleached wool fabric (2/24.75<sup>d</sup>×2/27.3<sup>d</sup> count, 39×11 threads/cm wrap× fill and 135 g/m<sup>2</sup> plain weave) and nylon fabric (20<sup>d</sup>×24<sup>d</sup> count, 52×38 threads/cm wrap × fill and 42.13 g/m<sup>2</sup> plain weave) were used.

#### Methods

#### Preparation of 4-methoxybenzeneazo – 2'-naphthol (dye 1) and 2-nitrobenzeneazo-2'-naphthol (dye 2)

The synthesis of azo-dye is a two step process. The first step is the formation of aromatic diazonium cation (ArN<sup>+</sup>≡N:) and the second step is the coupling reaction between this cation and phenolic substrate. Both steps are pH dependent. The reaction scheme with possible mechanism is described in Figures 1 and 2.



### Determination of physico – chemical properties of synthesized dyes

Melting points of dyes 1 and 2 were measured on electrically operated melting point apparatus of Sunder Industrial Products, Mumbai, India and were uncorrected. The UV-VIS absorption spectra were recorded in Perkin – Elmer Lambda 40 (UV- VIS) spectrophotometer in ethanol. The infrared spectra were recorded on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr discs ( $4000 - 400 \text{ cm}^{-1}$ ). Elemental analyses (C, H, N, O) were carried out using a Perkin-Elmer 2400 II elemental analyser. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were taken on a Bruker 300 MHz FT-NMR spectrometer using trimethyl silane as an internal standard in  $\text{CDCl}_3$  for dyes 1 and 2. LC-MS Thermo Finnigan navigator 30019 was used for recording the mass spectra.

### Dyeing of wool and silk

The dye (0.2g) was pasted with warm water and then 80 ml of boiling water was added and stirred to give a clear solution. The resulting dye solution was made upto 100 ml with boiling water. The dye bath was made up of the dye solution (20 ml), acetic acid (2ml of 10%), Glanbers Slat (2 ml of 20%) and water (16 ml). The wool fabric (2g) was watered and immersed in the dyebath at  $50^\circ\text{C}$ , then the temperature was raised to  $75^\circ\text{C}$  over 20 minutes and dyeing was continued for 45 minutes at  $75^\circ\text{C}$ . The pH was adjusted to 3.0 with acetic acid. The dyed material was taken out of the dyebath, washed with cold water twice for 10 minutes, soaped with Iodet T ( $2\text{g l}^{-1}$ ) in a bath containing water (material to liquor ratio, 1:20) at  $50^\circ\text{C}$  for 20 minutes followed

by washing thoroughly with cold water and drying in air [8]. To dye silk fabric, the dye bath was made in a manner similar to that described above for wool fabric.

### **Dyeing of nylon**

A different dye bath was prepared. It was made up by mixing the dye solution (similar method to previous fabrics) (20 ml) with Lenacid NL (1.2 ml of 10%) as an acidic buffer (pH 5 to 5.5) and water (18 ml). The Nylon fabric (2g) was wetted and immersed in the dye bath at 40°C. The bath temperature was then raised to 102°C over 15 minutes and maintained for 30 minutes. At this temperature formic acid (1.5 ml of 10 %) was added to the dye bath to achieve good exhaustion (Dakiky and Meincova, 1999). After cooling of the dye bath, the dyed fabric was rinsed and reduction – cleared twice with Iodet T (2 gL<sup>-1</sup>) in a bath containing water (material to liquor, 1:2) at 40°C for 15 minutes followed by washing thoroughly with cold water and drying in air.

### **Determination of physico-chemical properties of dyed fabrics**

Rubbing, washing and light fastness were determined using ISO-105-AO3, ISO-105-AO2, ISO-105-BO1 methods (International standard ISO-105-AO3, 105-AO2-1978 and 105-BOI-1978). The exhaustion (%), fixation (%) and realization (%) of the dyed samples were determined as per the method described in the literature [9].

### **Determination of antibacterial activity**

Antibacterial activity of the synthesized dye compounds was determined *in vitro* by standard agar well diffusion method [10] against various gram-negative and gram-positive bacteria at a concentration of 200 µg/100 µL in DMSO solution.

### **Kinetics of azo dye oxidation**

Organisms (5 to 30 µg), dialyzed against 10mM phosphate (pH 6.5), was incubated with an azo dye (50 µM) in 10mM phosphate buffer (pH 6.5; 1ml) saturated with oxygen. Dye oxidation was determined by monitoring the loss of absorbance at  $\lambda_{\max}$  with a spectrophotometer.

## **Results and Discussion**

### **Physical properties of dyes**

Azo dyes so prepared were found as red coloured needle shaped crystals (dye 1) and reddish orange coloured fine powdery crystals (dye 2). The TLC results showed that only a single spot was observed for each dye.

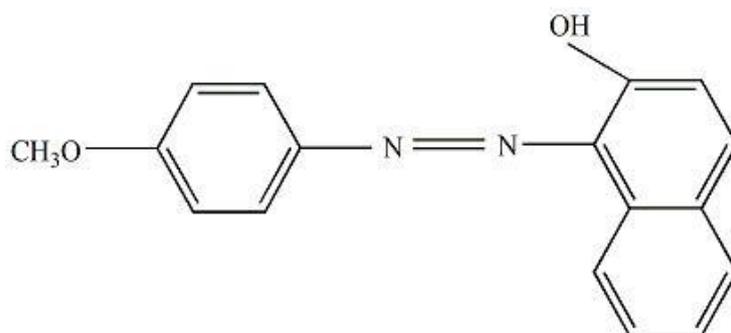
The results of elemental analysis and spectral data of each synthesized dye as shown in Tables 1 and 2 were consistent with the predicted structure (Fig. 3).

**Table 1.** Elemental data for synthesized dyes

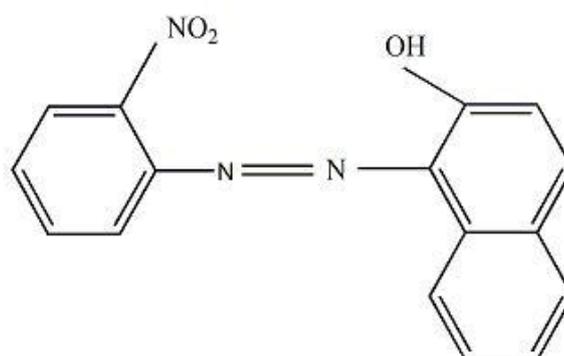
Name	Empirical formula	Yield (%)	m.p. (°C)	R <sub>f</sub>	Mol. Wt	%C		%H		%N		%O	
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Dye 1	(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> )	80	186	0.79	278	73.40	73.10	5.03	5.23	10.07	10.04	11.50	11.63
Dye 2	(C <sub>16</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> )	90	281	0.86	293	65.56	65.33	3.75	3.67	14.33	14.13	16.40	16.87

**Table 2.** Spectral data of synthesized dyes with assignments

Dye	IR Bands		NMR Signals		Mass (m/z)
	Frequency (cm <sup>-1</sup> )	Characteristics	<sup>1</sup> H NMR δ/ppm	<sup>13</sup> C NMR δ <sub>c</sub> /ppm	
Dye 1	3434 1598 1499 1441 1244 1026	Phenolic-OH Around Arm. C=C Arm. N=N Arm. Ar-O O-CH <sub>3</sub>	15.69( <sup>1</sup> H,s,OH) 8.67(1H,d,J8.1H <sub>2</sub> ,Ar-H) 7.79-7.65(4H,m,Ar-H) 7.59-7.53(1H,m,Ar-H) 7.41-36(1H,m,Ar-H) 7.04-6.96(3H,m,Ar-H) 3.81(3H,s,O-CH <sub>3</sub> )	161.22 160.54 141.71 136.56 133.22 129.45 128.12 124.68 121.94 114.64 55.50	278.9(M <sup>+</sup> )
Dye 2	3439 1607 1559 1481	Phenolic OH C=C Ar-NO <sub>2</sub>	16.59(1H,s,-OH) 8.42-8.09(3H,m,Ar-H) 7.76-7.12(6H,m,Ar-H) 6.81-6.65(1H,m,Ar-H)	181.20 143.44 139.33 135.56 133.10 129.70 129.09 127.81 127.13 126.26 123.56 122.96 117.77	293.9(M <sup>+</sup> ,58%)



4- methoxybenzeneazo- 2'- naphthol(dye 1)



2- nitrobenzene- 2'- naphthol(dye 2)

**Figure 3. Structure of dyes 1 and 2**

The number of azo groups is one for each dye. The nitrogen content and the number of azo groups for each dye are correlated with each other as obtained from molecular weight determination. The IR spectrum of each dye exhibited the important features of aromatic, azo, phenolic-OH, methyl oxide, and nitro groups. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra also showed the important signals at their expected positions for the dye compounds based on the p-anisidine and 2-nitroaniline and their reactive sites for azo coupling. The structures of the azo dyes shown in Figure 3 were thus confirmed.

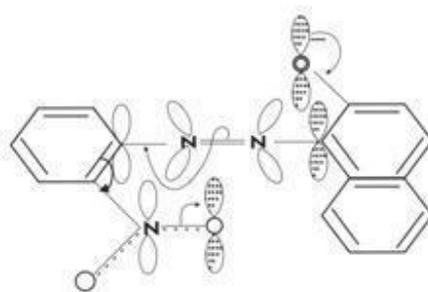
Mass spectra of the synthesized dyes (dyes 1 and 2) showed molecular ion peaks [M<sup>+</sup>] at different intensities (Table 2) which confirmed their molecular masses. In case of dye 1, the tallest peak at 44 amu (atomic mass unit) corresponded to the C<sub>2</sub>H<sub>6</sub>N<sup>+</sup> ion (M-44). The other peaks such as M-278.9 (C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>), M-127(C<sub>10</sub>H<sub>7</sub><sup>+</sup>), M-159(C<sub>10</sub>H<sub>9</sub>ON<sup>+</sup>) and M-105 (C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup>) were fragment ions derived from the parent ion. Dye 2 also showed highest peak at 44 amu corresponded to the positively charged C<sub>2</sub>H<sub>6</sub>N<sup>+</sup> ion (M-44). The other peaks like M-293.9 (C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>), M-127 (C<sub>10</sub>H<sub>7</sub><sup>+</sup>), M-159 (C<sub>10</sub>H<sub>9</sub>ON<sup>+</sup>) and M-105 (C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup>) represented the cations produced by the breakdown of the dye 2.

The absorption maxima (λ<sub>max</sub>) in the visible spectra of the dyes recorded in C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O system were 469.5 and 486.0 nm as shown in Table 3.

**Table 3** Absorption maxima ( $\lambda_{\max}$ ), molar extinction co-efficient ( $\epsilon$ ), intensity ( $\log\epsilon$ ), charge transfer ( $h\nu_{\text{ICT}}$ ), exhaustion (E), and fixation (F) of synthesized dyes on wool, silk, and nylon fabrics

Dye	Absorption maxima ( $\lambda_{\max}$ ) (nm) in ethanol ( $\epsilon$ )	Intensity ( $\log\epsilon$ )	Charge transfer ( $h\nu_{\text{ICT}}$ ) (eV)	Dyeing of wool		Dyeing of silk		Dyeing of nylon	
				%E	%F	%E	%F	%E	%F
Dye1	469.5 (30923)	4.4903	2.64	82.3	90.1	80.2	87.8	75.5	83.1
Dye2	486.0 (27750)	4.4433	2.55	86.0	96.8	82.5	93.1	78.2	85.0

The value of the logarithm of the molar extinction coefficient ( $\log\epsilon$ ) of dyes 1 and 2 were 4.4903 and 4.4433 which are constant with their high absorption intensity. Moreover, the presence of electron donating or electron attracting groups did not bring about mark increase or decrease in  $\lambda_{\max}$  in the visible region and  $\log\epsilon$  remain nearly constant. However electron donating or attracting substituents, such as  $-\text{OCH}_3$  or  $-\text{NO}_2$  in the coupler increase the polarizability. This leads to a decrease in the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and thus  $\pi$  (HOMO) -  $\pi^*$  (LUMO) electronic transition occurs with lower frequency photons, resulting in a bathochromic shift of the visible absorption band [11].

**Figure 4. Electron flow from naphtha - oxygen to benzonitro-oxygen via azo group**

### Dyeing properties of the synthesized dyes

The exhaustion of the dye bath and the fixation of dye on nylon fabric were comparatively lower than that of wool and silk fabrics. This is due to comparatively higher cohesive energy density of nylon polymer chain molecules and the lower para electro-negativity of the terminal polar groups which ultimately hinders the affinity and penetration of the dye molecules to some extent [12]. In spite of the higher molecular weight dye 2 showed comparatively good exhaustion and fixation behaviour than dye 1 due to its solubilizing and less aggregated character. Moreover dye 1 specially responded to fluorescence. Quantum yield and  $\lambda_{\max}$  of dye 1 molecule was found to be 0.011 and 585 nm.

The dyes were applied at 2% depth on wool, silk, and nylon fabrics. These dyes gave bright red, bright orange and reddish brown shades with a good levelness, brightness, and depth on the fabrics. The variation in the shades of the dyed fabrics results from both the nature and position of the substituent present on the diazotized compounds. The dyeing showed an excellent fastness to light and washing with good fastness to rubbing. A remarkable degree of level in surface area after washing was observed. This may be attributed to the good penetration and affinity of the dye to the fibre structure.

**Table 4.** Fastness properties of the dyes on wool, silk, nylon fabrics

Dye	Color	Types of fabrics	Washing fastness	Rubbing fastness		Light fastness
				Dry	Wet	
Dye 1	Brilliant red	Wool	5	4-5	4-5	5
		Silk	5	4-5	4-5	5
		Nylon	4-5	4	4	5
Dye 2	Reddish orange	Wool	4-5	4	4-5	6
		Silk	4-5	4-5	4-5	6
		Nylon	4	4	4	6

**Antibacterial activity**

Antibacterial activities and oxidation kinetics of dyes 1 and 2 were monitored against four strains (Table 5).

**Table 5.** Antibacterial activity and oxidation kinetics of synthesized dyes

Dye no.	$\lambda_{\max}$ (nm) ( $\epsilon$ , $\text{mM}^{-1} \text{cm}^{-1}$ )	Rate of oxidation (anti bacterial activity)			
		Bacillus subtilis	Escherichia coli	Salmonella typhi	Staphylococcus aureus
Dye 1	469.5 (1.45)	2.72 (-)	2.71 (-)	2.68 (-)	2.67 (-)
Dye 2	486.0 (1.28)	2.17 (-)	2.22 (-)	2.39 (-)	2.34 (-)

Diameter of inhibition zone in mm : 12-16; Concentration : 100ug/mL; (-) : inactive ;

$\lambda_{\max}$  (nm) was measured in 10 mM phosphate solution

The results showed that both the dyes exhibited very slow rate of oxidation and inhibited bacterial growth. This can be attributed to the fact that enriched electron cloud of naphtha moiety arising from electron donating power of O<sup>-</sup> centre could actually be drifted to nearby vacant  $\pi^*$

orbital of azo (N=N) group [13]. Amongst the two synthesized dyes the rate of oxidation of dye 2 was comparatively lower than that of dye 1 as dye 2 possesses a strong electron withdrawing group  $-\text{NO}_2$ , the electron density in the diazotized benzene nucleus is further reduced (Figure 4) and consequently the rate of oxidation of the dye was subsequently reduced. This might also be the cause of its more antibacterial effect.

### Conclusion

Two brilliant azo dyes were successfully synthesized by standard methods of diazotization and coupling using little variation of pH maintenance and methods of crystallization. Brilliant crystals of 4-methoxybenzeneazo-2'-naphthol and 2-nitrobenzeneazo-2'-naphthol were isolated and characterized by a number of spectroscopic methods. The results on the elemental analysis and spectral studies of each dye were consistent and hence confirm the predicted structure. The synthesized dyes showed excellent fastness to light, washing with good fastness to rubbing. They also showed remarkable levelness after washing. The nature of the substituents in the coupling components also showed little influence on the visible absorption and the shade of the dyeing. The results showed that both the dyes exhibited very slow rate of oxidation and also inhibited bacterial growth but the rate of oxidation of dye 2 was comparatively lower than dye 1 and hence resulted more antibacterial effect.

### References

1. Zollinger, H., *Color Chemistry-Synthesis, Properties and Application of Organic Dyes and Pigments*, VCH publishers, New York, 1987, 92-102.
2. Maynard, C. W., *Riegel's Handbook of Industrial Chemistry*, 3rd ed. Van Nostard Reinhold, New York, 1983, 809-861
3. Catino, S. C and Farris, R. E., *Concise Encyclopedia of Chemical Technology*, M. Grayson Ed., John Wiley & sons, New York, 1985,142.
4. Peters, A. T. and Freeman, H. S., *Colour Chemistry-The Design and Synthesis of Organic dyes and Oigments*, Elsevier Applied Science Publishing, Baraking Essex, U. K., 1991, 193-195.
5. Kocaokutgen, H., Erdem, E. and Guemriikcuekcueoglu, I. E., Synthesis of HFAN and its chromium and cobalt complexes and their application on Nylon 6 and wool, *J. Soc. Dyers Color*, 1998,114, 93-95.
6. Freeman, H. S. and Sokolowska, J., Developments in dyestuff chemistry, *Rev. Prog. Color.*, 1999, 29, 8-21.
7. Dakiky, M. and Memcova, I., Aggregation of o,o'- dihydroxyazo dyes, I: Concentration, temperature and solvent effect, *Dyes Pigments*, 1999, 40, 141-150.
8. Sekar, N. and Tiwari, P. S., Synthesis of symmetrical bis azo acid dyes using 1H, 5H-pyrazoleo-[1,2- $\alpha$ ]-pyrazole 1,3,5,7 (2H, 6H)-tetrone, *Colourage*, July, 2007, 73-74.
9. Kaur, S. and Singh, P.P., Eichhoria ash as an adsorbent for colour reduction of acid dyes from aqueous solutions, *Colourage*, March, 2007, 52-56.
10. Chung, K. T. and Cerniglia, C. E., Mutagenicity of azo dyes: structure-activity relationships. *Mutat. Res.* 1992, 277, 201-220.
11. Dixit, B. C., Patel, H. M. and Desai, D. J., Synthesis and application of New mordant and disperse azo dyes on 2,4-dihydroxy benzophenone, *J. Serb. Chem. Soc.*, 72 (1), 2007,110-127.
12. Faraqui, F. I., Sheikh, M. R. K. Hossain, M. I. and Saha, S. K. Selection of optimum dyeing conditions in dyeing Jute fibre with reactive dyes and their color fastness properties, *Ind. J. Chem. Technol.*, 1997, 4, 185.
13. Spadaro, J. T. and V. Renganathan, Peroxidase-catalised oxidation of azo dyes: mechanism of disperse yellow 3 degradation, *Arch. Biochem. Biophys.*, 1994, 312, 301-307.