ISSN 214-453-2

SYNTHESIS AND CHARACTERISATION OF AZO DYES DERIVED FROM NAPHTHALEN-2-OL AND THEIR WASHFASTNESS PROPERTIES ON COTTON, WOOL AND NYLON FABRICS

A. C. MELA[1], S. M. UMAR[2] AND A. GIWA[1]*

[1*]Department of Polymer and Textile Science, Ahmadu Bello University, Zaria, Nigeria

[2]Petrochemical and Allied Division, National Research Institute for Chemical Technology, Basawa, Zaria, Nigeria

[agiwa@abu.edu.ng; +2348037033052]

ABSTRACT

A series of azo dyes was synthesised by coupling reaction of napththalen-2-ol with diazotized 4-sodiumphenolate, 4-Nitrophenylazo and 4-Chlorophenylazo respectively, as diazo components. The characterization of the dyes was carried out by GC/MS analysis. The solubility of dyes in the visible absorption spectra was also determined. The dyeing performances of the three dyes were assessed on cotton, wool and nylon fabrics, also determined are the molar absorbtivity, dyebath exhaustion (%E) and dye fixation (%F). The dyed fabrics show very good washing fastness properties for wool and nylon and moderate for the cotton fabric. These dyes were found to give bright yellow to purple colour shades with very good depth and levelness on the fabrics. The dyebath exhaustion and fixation on the various fabrics were also found to be very good.

Keywords: *Diazotization, coupling, dyeing, exhaustion, fixation, fastness.*

INTRODUCTION

Azo compounds constitute the largest and the most diverse group of synthetic dyes with application not only as textile colourants but in many other industrial fields for colouring different substrates, biological-medical studies, in the field of non-linear optics and optical data storage [1, 2, 3].

Out of different classes of dyes, azo dyes constitute the largest group of colourants used in industry [3]. Azo dyes do not occur in nature and are produced only through chemical synthesis [4]. 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, ink–jet printers etc [5].

Azo compounds are compounds bearing the functional group R-N=N-R', in which R and R' can be either aryl or alkyl. IUPAC defines azo compounds as: "Derivatives of diazene (diimide), HN=NH, wherein both hydrogens are substituted by hydrocarbyl groups, e.g. PhN=NPh azobenzene or diphenyldiazene." The N=N group is called an azo group. Most coloured textile and leather articles are treated with azo dyes and pigments.

Azo dyes are made by the combination of two or more compounds formed by the following process; Diazotization and then coupling. The process of forming diazonium compounds is called diazotization, diazotation or diazoniation. The most important method for the preparation of diazonium salts is treatment of aromatic amines such as aniline with nitrous acid. Usually the nitrous acid is generated in situ (in the same flask) from sodium nitrite and mineral acid. In aqueous solution diazonium salts are unstable at temperatures above +5 °C; the $-N^+\equiv N$ group tends to be lost as N_2 (nitrogen gas). The reaction involved can be represented by the equation:

$$AR - NH_2 + 2HX + NaNO_2 \rightarrow AR - N^+ \equiv NX^- + 2NaX + H_2O$$

(X=Cl, Br, NO_3, HSO_4, etc)

An azo coupling is an organic reaction between a diazonium compound and a dialkylaniline ($C_6H_5NR_2$), phenol or other aromatic compound which produces an azo compound. In this reaction the diazonium salt is an electrophile and the activated arena is a nucleophile in an electrophilic aromatic substitution. In most cases, the diazonium compounds are aromatic. The product will absorb longer wavelengths of light than the reactants because of increased conjugation. Aromatic azo compounds tend to be brightly coloured due to the extended conjugated systems; many are used as dyes.

A vast amount of work has been reported on aminothiazole based dyes in the last decade [6, 7, 8, 9]. But so far, little or no work has been done on the synthesis of one simple azo dye suitable for cotton, wool and nylon fibres. The present study focused on the synthesis and characterization of azo dyes derived from Naphthalen-2-ol and investigation of their application on cotton, wool and nylon fabrics.

EXPERIMENTAL

Materials and Methods

Both the chemicals and the coupling components used were of commercial grade. The chemicals obtained from the Department of Textile Science and Technology, Ahmadu Bello University, Zaria, Nigeria, were used as received, except that the coupling

components were further purified by recrystallization before use. All the solvents used were of spectroscopic grade. The melting points were determined by open capillary method, and the visible absorption spectra were measured using a UV/Vis spectrophotometer. Purification of the products was done using TLC (1 mm thickness glass plates 20x5 cm), using suspension of silica gel G in $CHCl_3$. The solubility of the synthesized dyes were determined in four solvents; distilled water, ethanol, acetone, and dimethylformamide (DMF). The percentage yield of each dye synthesized was calculated with the equation I below:

$$Dye\ yield\ (\%) = \frac{actual\ yield}{theoritical\ yield} \times 100 \qquad \ldots \text{I}$$

The molar extinction coefficient (molar absorbtivity) of each dye synthesized was calculated using Equation II and III:

$$\varepsilon = \frac{A}{CL} \quad \ldots \text{II} \qquad\qquad A = \log \frac{L_0}{L_1} \quad \ldots \text{III}$$

where: ε=molar extinction coefficient, A=Absorbance at λ_{max}, C=Concentration in mol/dm^3, L=Path length of cell (1cm), L_0=intensity of incident light and L_1=intensity of transmitted light.

The optical density of each dye bath before and after dyeing was determined and the maximum absorption wavelengths were recorded and the percentage exhaustion of the dye processes was calculated with the equation IV:

$$Exhaustion\ (\%) = \frac{OD_1 - OD_2}{OD_1} \times 100 \quad \ldots \text{IV}$$

where: OD_1=optical density before dyeing and OD_2=optical density after dyeing.

The wash fastness properties were determined in accordance with IS:765-1979. The procedure of the method of colour fastness tests was as described in the literature [6].

Preparation of Intermediates

Diazotisation of aminobenzoic acid: Approximately 0.5ml of conc. HCl was placed in 100ml beaker A, and then placed in an ice water bath. 0.49g of aminobenzoic acid was poured into beaker B, and 0.13 g of sodium carbonate (Na_2CO_3), and 5 ml of water were added. It was placed in a hot water bath until a clear solution is obtained. In beaker C, a solution containing 0.2g of sodium nitrite ($NaNO_2$) and 1ml of water was prepared. Beaker B was removed from the hot water bath and all the contents poured at once from beaker C into beaker B. The contents from beaker B were added to beaker A and place in an ice water bath until a significant amount of solid has precipitated.

Diazotisation of nitroaniline: 1.5ml of water and 1.5ml of conc. HCl was poured in a beaker and placed in an ice water bath. In a 25ml round bottom flask, 0.7g of nitroaniline, 0.38g of sodium nitrite ($NaNO_2$), 1.5ml of water was also poured and a magnetic stir bar. The contents were stirred rapidly using a stirrer/hotplate. The beaker was removed from the ice water bath and the round bottom flask was placed in the bath. The content of the beaker were added to the round bottom flask and was stirred gently for 10 minutes. The solid were filtered into a beaker using a glass funnel and a small cotton plug.

Diazotisation of Chloroaniline: 1.5ml of water and 1.5ml of conc. HCl was poured in a beaker and placed in an ice water bath. In a 25ml round bottom flask, 0.7g of chloroaniline, 0.38g of sodium nitrite ($NaNO_2$), 1.5ml of water was poured and a magnetic stir bar. The contents were stirred rapidly using a stirrer/hotplate. The beaker was removed from the ice water bath and the round bottom flask was placed in the bath. The content of the beaker were added to the round bottom flask and was stirred gently for 10minutes. The solid were filtered into a beaker using a glass funnel and a small cotton plug.

General Coupling Procedure

In a 25ml round bottom flask with a magnetic stir bar, 0.74g of Naphthalen-2-ol was dissolved in 10ml of 2.5M NaOH and place in an ice-water bath. The content of the beaker was slowly added while stirring and continue stirring for 10 minutes while in the ice-water bath. 1.5ml of conc. HCl was slowly added then 1g of NaCl and the round bottom flask was heated with a water bath until dissolved. The reaction was cooled to room temperature then placed in an ice-water bath for 15 minutes. The solid was filtered using vacuum filtration with a Buchner funnel and washed with 5 ml of water to give dye 1. The same procedure was repeated for the preparation of the dye 2 and 3.

Dye application on cotton, wool, and nylon fabric

The dye bath was prepared using a liquor ratio of 40:1, and percentage shade of 5%. Each of the synthesized dyes was applied on the respective fabrics by exhaustion dyeing. The dyeing of the respective fabrics was carried out according to method described in the literature [10]. After dyeing, the fabric was removed, rinsed thoroughly in running cold water and dried. The procedure was repeated for each dye, but at different dyeing time, of 30, 45, and 60 minutes. The optical density was measured before and after dyeing and the percentage exhaustion calculated for each time. The dyebath exhaustion (%E) and dye fixation (%F) of the dye on the fabric was determined according to the standard method [11].

RESULT AND DISCUSSION

Characteristics of the synthesized dyes

On diazotization of each of aminobenzoic acid, nitroaniline and chloroaniline, which were respectively coupled with Naphthalen-2-ol, gave three different dyes and some of the physico-chemical characteristics of the dyes obtained are shown in table 1.

Table 1: Absorption maxima, intensities, characterization data, exhaustion and fixation of the dyes

Characteristics	Dye 1	Dye 2	Dye 3
Wave length of maximum absorption (λ_{max}) (nm)	420	492	524
Absorbance	1.1895	1.0583	1.5437
Extinction coefficient ($mol^{-1}cm^{-1}$)	11895	10583	15437
Molecular weight (g/mol)	314.00	293.28	282.72
Colour observed	Yellow	Red	Purple
Melting point (°C)	251.00	291.00	280.00
Yield (%)	54.90	79.20	60.70
Solubility in various solvents			
Distilled water	Sparingly Soluble	Sparingly Soluble	Sparingly Soluble
Ethanol	Soluble	Soluble	Soluble
Acetone	Soluble	Soluble	Soluble
DMF	Soluble	Soluble	Soluble

As seen in Table 1; all the three synthesised dye products are found to melt between 251°C - 280°C. The very close range of melting temperatures may be attributed to the similarity in their chemical structures. However, the little variations could be due to the variation in molar mass of the repeat units and the molecular mass of the polymers [12].

The solubility properties of the synthesized dyes are also summarized in Table 1. The products are soluble in most of the solvents used for the test, except in distilled water where they are all sparingly soluble. Solubility of the polymeric dyes in polar organic solvents could be attributed to the presence of the OH group. The slight solubility in water is also attributable to hydrogen bonding between the groups in the dye and hydroxyl groups in water [12].

The azo dyes obtained were found to exhibits colour Yellow (Dye 1), Red (Dye 2) and Orange (Dye 3) with the following corresponding wave length of maximum adsorption of 420nm, 492nm and 524nm respectively. Absorption maxima (λ_{max}) values tend to be related to the strength of the electronic withdrawing or donating power in the benzenoid system [13]. Since the electronic transitions in these compounds involves a general migration of electron density from the donor group toward the azo group, the greatest effect in terms of longer wavelength is achieved by placing the substituents in the positions ortho or para to the azo group for effective conjugation [14, 15]. The TLC results showed that only a single spot was observed for each dye. The results of the GC/MS were consistent with the predicted structures as shown in figure 1.

Synthesised Dye 1, 2 and 3

The general coupling procedure of the different diazonium salts produced the following dye 1, 2 and 3 respectively as shown in figure 1. The GC/MS identified Dye 1 as 1-[(4-sodiumphenolate) azo]-2-naphthol, Dye 2 as 1-[(4-Nitrophenyl) azo]-2-naphthol and Dye 3 as 1-[(4-Chlorophenyl) azo]-2-naphthol.

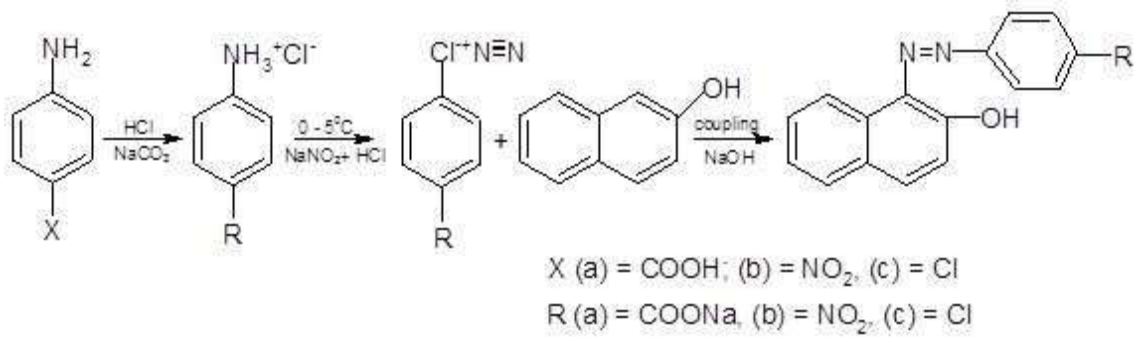

Figure 1: Reaction scheme for the synthesis of dye 1, 2 and 3

Effect of time on dye exhaustion

Figure 2, 3, and 4 shows the effect of time on dye exhaustion on cotton, wool, and nylon respectively. The rate of dyeing increases as time increases, as well as the rate of dye bath exhaustion reduces as time increases. From figure 2, cotton shows good dye exhaustion on dye 1, than dye 3, which also shows a better exhaustion than dye 2, as time increases. The three dyes shows point of maximum exhaustion at time 50 minutes. From figure 3, wool shows good dye exhaustion on dye 3, than dye 1, which also shows a better exhaustion than dye 2, as time increases. The three dyes shows point of maximum exhaustion at time 60 minutes. From figure 4, nylon shows good dye exhaustion on dye 2, than dye 3, which also shows a better exhaustion than dye 1, as time increases. The three dyes shows point of maximum exhaustion at time 50 minutes.

The exhaustion phenomena is similar to works of Bradbury *et al*. [16] which states that in the presence of salts, substantivity is increased due to free site for bonding, aggregation of dyes into the fibre, facilitated

by temperature rise. This increase attains a limit and aggregation maintains a drop in exhaustion for time above 60 min. This may be due to decrease in dye molecular stability, gradual equilibrium and saturation condition of the substrate [17]. This result showed a rapid uptake of dyes during the initial 20 min due to better dye molecular affinity and diffusion with fabrics. This observation agrees with Bilmeyer and Saltzman [11]. Also dyeing at lower temperature prolongs percentage exhaustion beyond 60 min [18].

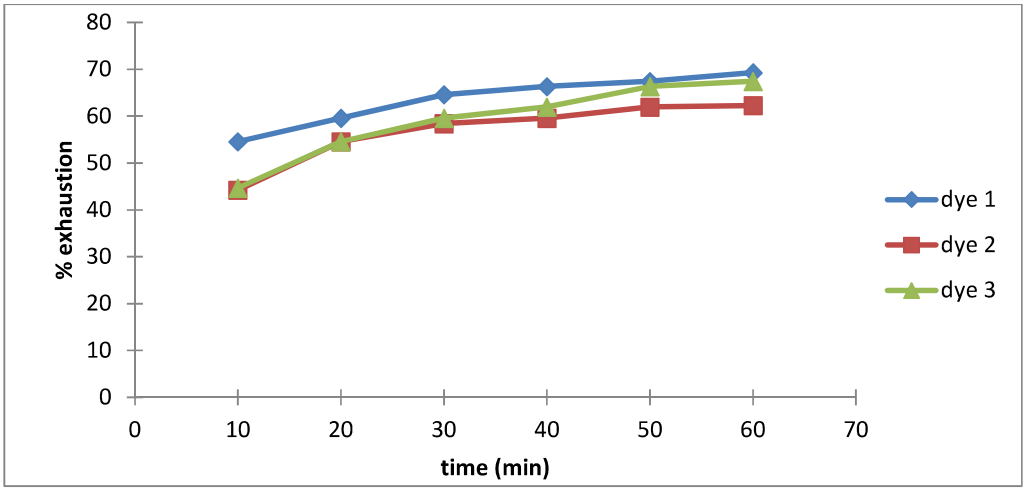

Figure 2: Effect of time on percentage exhaustion of dyes on cotton

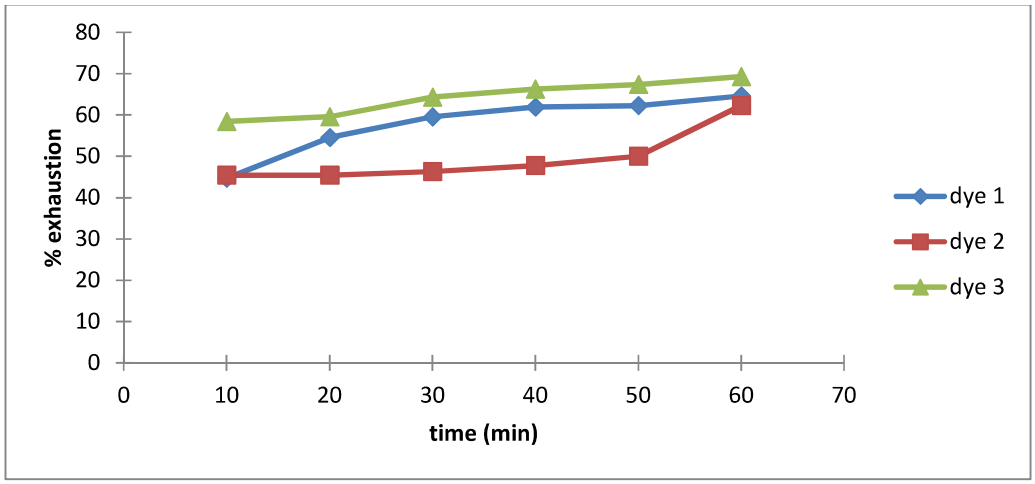

Figure 3: Effect of time on percentage exhaustion of dyes on wool

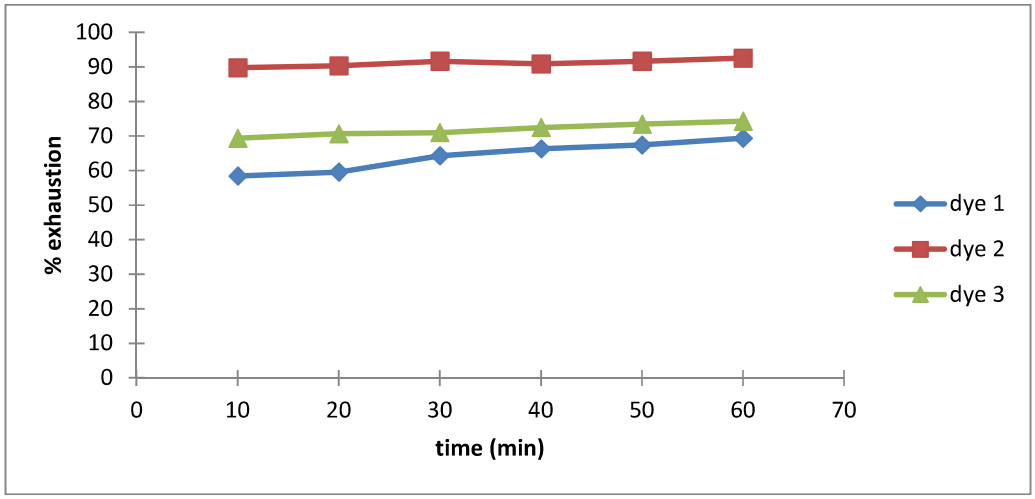

Figure 4: Effect of time on percentage exhaustion of dyes on nylon

Wash fastness test

Table 2 shows the results of the washing fastness test (ISO III) of the synthesised dyes on cotton, wool, and nylon respectively. The wash fastness of dye 3, as shown in the Table 2, is better than dye 1, and 2, which shows a moderate change in shade of the dyed fabrics. While their staining on washing is also moderate. The wash fastness of the three dyes on wool, all gives a good change in shade of the dyed fabric, and also a moderate staining on washing. The wash fastness of dye 1, as shown the Table 2, is better than dye 2, and 3, which shows a moderate change in shade of the dyed fabrics. While their staining on washing is also moderate. Wash fastness property depends upon the solubility of dye in water, type of linkage present in dye molecule and fiber, size of dye molecules and charge present on the dye. All the 3 synthesised azo dyes 1 – 3 showed very good wash fastness properties according to the international geometric gray scale. This result may be attributed to the sparingly insolubility of the dyes in water. Staining against the respective attached fabrics also gives very good ratings, as both fabrics remain unstained.

Table 2: Wash fastness ratings of dye 1, 2 and 3

dyes	Change in shade			Stain on undyed fabric		
	cotton	wool	nylon	Cotton	wool	nylon
1	3	4	4	3-4	3	3
2	3	4	4	3-4	3	3-4
3	4	3	4	3	3	3-4

CONCLUSION

The results of dyeing of cotton, wool, and nylon with the three synthesized dyes shows that the dyes are applicable directly to cotton, wool, and nylon. The dyes have good levelness and penetration in wool and nylon, as well as high wash fastness, as compared to the dyes on cotton. Dyeing the fabrics with these dyes requires a careful and control environment, such as pH, temperature, time, and concentration, to enhance better penetration and migration (levelling) of the dyes into the fibre.

REFERENCES

1. GREGORY P. IN: HUNGER K, editor. Industrial dyes: chemistry, properties and applications. Weinheim: Wiley-VCH; 2002. p. 543–85.
2. CLARK RJH, HESTER RE. Advances in materials science spectroscopy. New York: John Wiley & Sons; 1991.
3. ZOLLINGER, H.,. Color Chemistry-Synthesis, Properties and Application of Organic Dyes and Pigments, VCH publishers, New York, 1991, 92-102.
4. MAYNARD, C. W., Riegel's Handbook of Industrial Chemistry, 3rd ed. Van Nostard Reinhold, New York, 1983, 809-861
5. CATINO, S. C AND FARRIS, R. E., Concise Encyclopedia of Chemical Technology, M. Grayson Ed., John Wiley & sons, New York, 1985,142.
6. PETERS, A. T. AND FREEMAN, H. S.,. Colour Chemistry-The Design and Synthesis of Organic dyes and Pigments, Elsevier Applied Science Publishing, Baraking Essex, U. K., 1991, 193-195.
7. KOCAOKUTGEN, H., ERDEM, E. AND GUEMRIIKCUEKCUEOGLU, I. E., (1998). Synthesis of HFAN and its chromium and cobalt complexes and their application on Nylon 6 and wool, J. Soc. Dyers Color, 114, 93-95.
8. FREEMAN, H. S. AND SOKOLOWSKA, J., (1999). Developments in dyestuff chemistry, Rev. Prog. Color., 29, 8-21.
9. DAKIKY, M. AND MEMCOVA, I., (1999). Aggregation of o,o´- dihydroxyazo dyes, I: Concentration, temperature and solvent effect, Dyes Pigments, 40, 141-150.
10. MARADIYA, H.R., PATEL, V.S. (2000). Synthesis of monoazo disperse dyes based on 2-aminoheterocycles and their dyeing performance on nylon fabrics. Journal of the Serbian Chemical Society, 65 (11), pp. 773-780.
11. BILMEYER, F.W. AND M. SALTZMAN, (1981). Principles of Colour Technology. John Wiley and Sons, New York, USA.
12. ROBERT T. M. AND ROBERT, N. B. "A Text Book of Organic Chemistry," Prentice Hall of India Private Limited, New Delhi, 2001, pp. 585-596.
13. PETERS AT. (1985). Substituent effects on the colour, dyeing and fastness properties of trisubstituted 4-N-b-Hydroxyethyl-N-b-Cyanoethylaminoazobenzenes. J Soc Dyers Colour; 101(11):361 – 367.
14. GRIFFITHS J. Colour and constitution of organic molecules. London: Academic Press; 1976.
15. SAWICKI E. (1957). Physical properties of the aminoazobenzene dyes. IV. The position of proton addition. J Org Chem; 22(4):365 – 367.
16. BRADBURY, M.J., P.S. COLLISHAW AND S. MOORHOUSE, (1995). Reactive dye selection and process development for exhaust dyeing of cellulose. Text. Chem. Colorist, 27: 19-23.
17. ASHOUR, S.S., (2010). Kinetic and equilibrium adsorption of methylene blue and remazol dyes onto steam-activated carbons developed from date pits. J. Saudi Chem. Soc., 14: 47-53.
18. GAMAL, A.M., S.A. ABO FARHA, H.B. SALLAM, G.E.A. MAHMOUD AND L.F.M. ISMAIL, (2010). Kinetic study and equilibrium isotherm analysis of reactive dyes adsorption onto cotton fiber. J. Am. Sci., 8: 95-110.