



Synthesis and Characterization of Monoazo Disperse Dye

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ABSTRACT

This work studied the use of 4-nitroaniline in the synthesis of monoazo dispersed. The 4-Nitroaniline was diazotized and coupled with 1-Naphthol, 2-Naphthol, Salicylic acid and Phenol to synthesize 4-[(4-nitrophenyl)azo]-1-naphthol, 1-[(4-nitrophenyl)azo]naphthalene-2-ol, 5-[(4-nitrophenyl)azo]salicylic acid and 4-[(4-nitrophenyl)azo]phenol respectively. The dyes were synthesized as solid crystals with good colouristic properties, with 87.60%, 64.20%, 67.90% and 47.30% yield and melting points of 261°C, 243°C, 294°C and 172°C respectively. The FTIR characterization of the dyes revealed the presence of C-O from phenol, C-N and N-H from amines, C-H from alkane, N=O from nitro compounds and -OH from alcohol and the proposed structures of the dyes revealed the presence of chromophoric, auxochromic and azodic groups which may help to explain why the dyes have excellent colourations. The UV-VIS absorption spectra of the dyes in methanol, ethanol and ethyl acetate revealed that the dyes have absorption bands within the visible region of the electromagnetic spectrum and that the λ_{max} of the dyes increases with increase in polarity of the solvents. The results also shows that dye 1 has the highest λ_{max} in solvents of different polarity. The dyeing and fastness properties of the dyes on nylon, wool, polyester and cotton revealed that the dyes will have commercial importance within the textile industries.

Key words: Dyes, UV, IR, 4-nitroaniline, monoazo

1.0 INTRODUCTION.

The use of attractive colourants for both social and economic reasons have always fascinated mankind (Roohi, 2019). From time antiquity, dyes and pigments have been used to impart colours to different commodities of commerce. A substance may be called dye, if it satisfies certain conditions as; it must have a suitable colour. It must be capable of being fixed on the fabric directly or with the help of certain agents called mordant. When fixed, it must not be fugitive, that is the colour must be fast to light and resistant to soap and water, and to a certain extent to dilute acids and alkalis (Sharma 2014).

A dye is a coloured substance that has the potential to form a chemical bond with the substrate to which it is being applied. It is used to impart colours to fabrics, leathers, papers and other materials such that the colouring is not easily affected by washing, heat, light or other factors to which the material is likely to be exposed (Buikinshaw, 2016). On the other hand, pigments do not chemically bind to the material they colour. pigments are finely ground solids dispersion in liquids. They are used mostly in the colouration of paints, printing inks and plastics, although they are applied to a certain extent in a much wider range of substrates including paper, textiles, rubber, glass, ceramics, crayons and building materials such as cement and concrete. In most cases, the application of pigments involves their incorporation into a liquid medium, for example a wet paint or ink or a molten thermoplastic material, by a dispersion process in which clusters or agglomerate of pigment particles are broken down into primary particles and small aggregates. The pigmented medium is then allowed or caused to solidify, by solvent evaporation, physical solidification or by polymerization, and the individual dye molecules are strongly attracted to the individual polymer molecules of the fibres to which they are applied, pigments are considered to have only a weak affinity for their application medium, and only at surface where the pigment particle is in contact with medium. (Christie R. M., 2002)

The Manufacture of virtually all commercial products involves colour at some stage and requires the addition of colouring agents like dyes or pigments. The different varieties of dyes in the market today is a consequence of the different range of tints and hues desired, the chemical nature of the materials to be coloured, and the fact that colour is directly related to the molecular structure of the dye.

Generally, dyes are classified into natural and synthetic based on the source of their origin. Natural dyes can be extracted from natural sources like flowers, fruits, leaves, roots, bark, etc., while synthetic dyes are generally synthesized in laboratories by the use of chemical substances. In addition, dyes can be classified according to their general structure into anionic, cationic, and non-ionic. They are also categorized based on application characteristics into ten different types (acidic, basic, mordant, reactive, direct, disperse, sulfur, pigment, vat, azo insoluble) (Ali, 2010)

The colour of a dye is dependent upon the ability of the substance to absorb light within the visible region of the electromagnetic spectrum (380-750 nm). An earlier theory known as Witt's theory (McGraw, 2003) stated that a coloured dye has two components, a chromophore (NO_2 , $-\text{CO}$, $-\text{N}=\text{N}$ - $\text{N}=\text{N}$ -

C=C- groups) which imparts colour by absorbing light within the visible region of the spectrum and an **auxochrome** (-OH, -NH₂, -NHR, -COOH, -SO₃H) which serves to deepen the colour of the chromogen. Other functional groups may be added which can modify or enhance the colour of the dye or to increase the solubility of the dye in water or attach the dye molecule to the fibres of the cloth (Buikinshaw, 2016).

This theory has been superseded by recent electronic structural theory which states that the colour in dyes can be attributed to the excitation of valence π -electrons by visible light (Bafana, 2011).

1.2 Components of Dye

Every dye comprises the following basic components; one or more fused benzene rings; chromophores, and auxochromes. Both auxochromes and chromophores are responsible for the colours of dyes (Sharma, 2011).

1.2.1 Chromophore

They are responsible for the appearance of colour in any dye. These chemical groups are known to be covalently unsaturated groups which are responsible for absorption in the ultraviolet or visible region (Sharma, 2011). Examples include -N=N-, -NO₂, -C=O, C=C, etc. It is worthy of note that chromophore does not itself determine the particular colour and hue of dye (Burkinshaw, 2016).

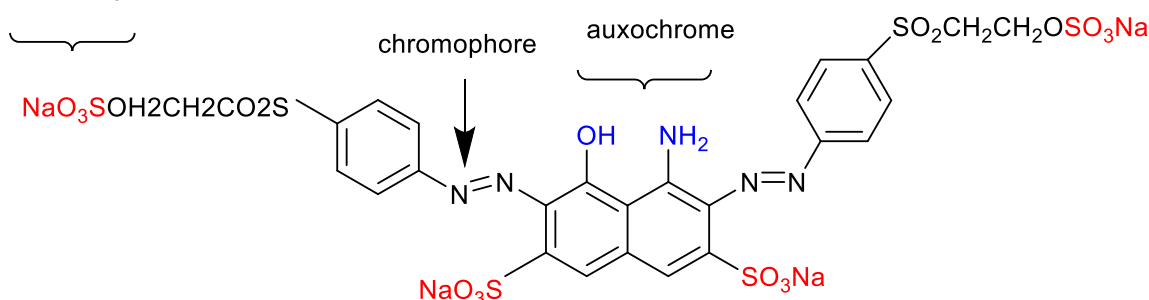
1.2.2 Auxochrome

This is a substituent group which is fused in a chromogen to influence its colour. Generally, auxochromic groups are capable of forming salts with acidic or basic group of a fibre, thus, they help the chromogen to fix permanently to the fibre (Sharma, 2011).

1.2.3 Chromogen

Chromogen can be defined as a chemical compound containing a chromophore. (Sharma, 2011). Chromophore and auxochrome(s) are also part of the chromogen (Taura, Gumel, Habibu and Adam, 2014; Carmen and Daniela, 2012).

water soluble group



Azo dyes are characterized by the presence of the azo moiety (-N=N-) in their structures. Usually, the azo group is attached to two radicals of which at least one but, more commonly, both are aromatic. They exist in the trans-form and the bond angle is approximately 120°; while the nitrogen atoms are sp² hybridized (Patil and Rajput, 2019).

They represent the largest group of coloured organic compounds, accounting for over 50% of all commercial dyes, and this is due to the number of variations in their chemical structures and their wide commercial applications (Mabrouk, Felaly, and El-Mossalamy, 2016).

Azo compounds are highly coloured and have been used as dyes and pigments for a long time (Pesyan, Gholsanamloo, Par, Rashidnejad, Gharib and Nejati, 2019). More importantly, azo compounds with two phenol rings separated by an azo bond are versatile molecules and have received much attention in research areas (Patel, Prajapati and Patel, 2013).

Most azo dyes are synthesized via the diazotization of appropriate primary aromatic amines and the coupling of the diazonium salt formed with one or more electron-rich nucleophiles such as amino and hydroxyl functional groups (Gürses, 2016). Other methods of synthesizing azo dyes include the reduction of nitroaromatic derivatives in alkaline medium, the reduction of nitroso compounds by aluminium lithium tetrahydride (AlLiH₄), oxidation of primary amines by potassium permanganate or lead tetraacetate, condensation of hydrazines and quinones, condensation of primary amines with nitroso derivatives, etc. (Zhao, 2011 and Leriche, 2010). In the synthesis of azo dyes, the azo group may form its bond with the benzene rings, naphthalene and aromatic heterocycles (pyridine) or to an aliphatic enolic group (Figure 1) (Towns, 1999). These help in the production of dyes with excellent colouristic properties with different shades of intensities.

2.0 Experimental

The monoazo disperse dyes were produced by the general methods of diazotization and coupling reactions as described by Sharma (2014).

2.1. General Methods for the Preparation of Diazonium Salt.

The diazonium salt was prepared by dissolving 1.73g (0.01M) of 4 – nitroaniline in 10 ml of conc. Hydrochloric acid. The mixture was stirred until the 4 – nitroaniline was completely dissolved. The mixture was gradually added with stirring into another beaker containing 20 ml of 2 M sodium nitrite (which has been previously cooled to below 5°C in an ice bath) to form a diazonium salt (Diazotization reaction). The mixture was allowed to remain in the ice bath to maintain the temperature at 5°C prior to the coupling reaction.

2.2. General methods of Coupling Reaction

In order to carry out coupling reaction, 1.38g (0.01 M) of the coupling agent (salicylic acid) was dissolved into a beaker containing 10 ml solution of 2 M sodium hydroxide. The mixture was stirred until complete dissolution was achieved. The beaker was immersed in an ice bath and the temperature allowed to cool below 5°C. While the content of the beakers were still below 5°C, the mixture was coupled by slowly adding the diazonium salt with constant stirring into the mixture of the salicylic acid using a dropping funnel. After the addition, the mixture was left in the ice bath for extra 10 minutes before filtration under vacuum. The solid product was re-crystallized by dissolving in a 30 ml of ethanol, heated to near boiling and allowed to cool to room temperature before immersing in an ice bath for re-crystallization. The solid product was filtered under vacuum, dried and weighed. The dye was stored in a small sample bottle prior to other analysis. These methods were used in synthesizing other dyes.

2.3 Dyeing of fabrics.

The dyeing process employed 1: 50 material to dye ratio. For cotton, wool and nylon, a fabric material weighing 1.0 g was wetted with water and the excess water squeezed off with a filter paper, after which, it was introduced into 50 ml of 2% dye solution which has been pre-heated to about 50°C. The mixture was allowed to be heated up to 100°C and the dyeing process continued for about 1hr. with occasional gentle stirring. After the dyeing process, the fabric was removed from the dye bath, rinsed with water, air dried and stored in a polyethylene bag prior to the fastness tests (Salah and El-Badry, 2012).

2.4 Dyeing of polyester fabric

Dyeing was carried out by using high temperature high pressure (HTHP) Method. Dyeing solution of 1% stock was prepared by dissolving 1.0 g of the dye in 100.0 g of dimethylformamide solvent. Material to liquor ratio of 1:50 was maintained all through the dyeing process. The fabric was immersed into the dye bath at 50°C after being wetted in the aqueous solution and dried. The temperature was increased to 130°C and dyeing continued at this temperature for 45 minutes while pH of 4.5 – 5.5 was maintained by using glacial acetic acid. The dyed sample was rinsed in cold water, air dried and presented for fastness tests (Ashitosh, Sandeep and Adivarekar, 2018)

2.5 Wash Fastness Test

The wash fastness was determined according to the International Standard Organization (ISO) washing test number 3. The dyed fabric measuring 10 X 5 cm was removed and treated at 60°C for about 45 minutes with a mixture that contains 0.5% of soap solution and 0.2% of sodium carbonate solution in the ratio of 50:1. After which, the fabric was washed in a running water and air dried. The change in shade of the material was related to the standard grayscale rating whose indications are 1 to 5 (where 1 is poor and 5 is excellent) (Ukponmwan, Odilora, Offor and Freeman, 1999)

2.6 Light Fastness

The light fastness test was carried by exposing the dyed fabric to sun light for about 35 hours and the change in shade of the material was evaluated according to the standard blue wool fabrics (grade 1 to 8) where 1 is poor and 8 is excellent. (Odilora and Omatseye, 2000).

2.7 Heat Fastness

The heat fastness examination was assessed according to ISO 105-PO1 1993. The dyed fabric was exposed to a heat source of about 170°C for 30 seconds and the change in shade was related to the standard grayscale (grade 1 to 5) where 1 is poor and 5 is excellent. (Odilora and Omatseye, 2000).

2.8 Determination of Wavelength of Maximum Absorption (λ_{max}) of The Dyes

The wavelength of maximum absorption of the dyes in methanol, ethanol and ethyl acetate were determined using Drawell D-8 UV-VIS spectrophotometer.

2.9 Determination of the Functional Groups Present in the Dyes

The functional groups present in the dyes were determined using Bulk Scientific M530 USA FTIR spectrophotometer.

2.10 Determination Molar Absorptivity of the Dyes.

The molar absorptivity of the dyes was determined according to the method described by Joseph (2020). The absorbance of 1M of the dye in a 1 cm cuvette (path length) was measured and the molar absorptivity calculated using the relationship:

$$A = \epsilon cl$$

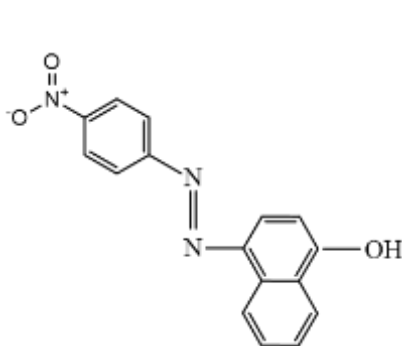
Where:

A = absorbance

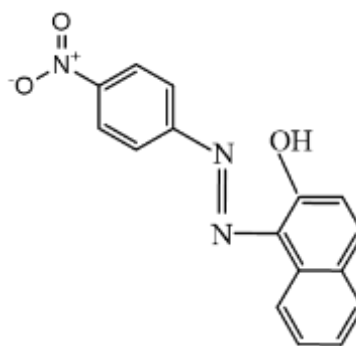
ϵ = molar absorptivity

C = concentration

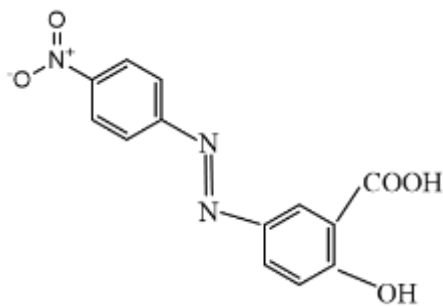
3.0 Results and Discussions



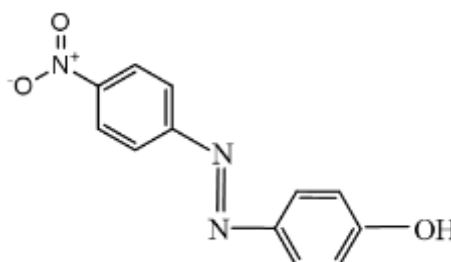
4-[(4-nitrophenyl)azo]-1-naphthol



1-[(4-nitrophenyl)azo] naphthalene-2-ol



5-[(4-nitrophenyl)azo]salicylic acid



4-[(4-nitrophenyl)azo] phenol.

The diazotization of 4-nitroaniline and subsequent coupling with 1-naphthol, 2-naphthol, salicylic acid and phenol produced monoazo disperse dyes with 87.6%, 64.2%, 67.9% and 47.3% yield respectively. The proposed structures of the dyes as shown in the figures above revealed the presence of $-\text{NO}_2$ and $-\text{N}=\text{N}-$ which represent the chromophoric and the azodic groups respectively, while the $-\text{COOH}$ and $-\text{OH}$ represent the auxochromic group. These explain why the dyes have brilliant maroon red, black, yellow and green colourations respectively. The dyes were synthesized as crystalline solid materials with melting points of 261°C, 243°C, 294°C and 172°C respectively.

Table 1.0: results of physical parameters of the synthesized monoazo disperse dyes.

Dyes	Molecular formula	MW	Melting point	% yield	Colour	Texture
Dye 1	$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3$	293	261	87.60	Maroon red	Powder

Dye 2	$C_{16}H_{11}O_3N_3$	293	243	64.20	Black	Crystalline
Dye 3	$C_{13}H_9O_5N_3$	287	294	67.90	Pantone 123 yellow	Powder
Dye 4	$C_{12}H_9O_3N_3$	243	172	47.30	Uniform green	powder

The results from table 1.0 above revealed that the dyes were synthesized as solid crystals with Maroon red, black, Pantone 123 yellow and uniform green colourations with 87.60%, 64.20%, 67.90% and 47.30% yield and melting points of 261°C, 243°C, 294°C and 172°C respectively.

Table 2: Wavelength of maximum absorption (λ_{Max}) and molar absorptivity of the synthesized monoazo dispersed dyes

Dye	Solvents	λ_{Max}
1	Methanol	575
	Ethanol	464
	Ethyl acetate	434
2	Methanol	407
	Ethanol	387
	Ethyl acetate	369
3	Methanol	432
	Ethanol	398
	Ethyl acetate	371
4	Methanol	436
	Ethanol	401
	Ethyl acetate	384
5	Methanol	456
	Ethanol	389
	Ethyl acetate	373

The UV-VIS absorption spectra of the dyes in methanol, ethanol and ethyl acetate are presented in table 2.0. The results revealed that the dyes show high λ_{max} of 575nm in methanol which is a more polar solvent than the ethanol and ethyl acetate where λ_{max} are 464nm and 444nm respectively for dye 1. This solvent effect on the λ_{max} of the dyes otherwise known as solvatochromism can be defined as the tendency of a substance to change colour due to a change in solvent polarity (Yusuf, Nkeonye, Bellow, Yakubu and Lawal, 2014).

This trend was also observed in all the dyes and the bathochromic effects observed in the λ_{max} of the dyes in the different solvents is as a result of the lowering of the energy level between $\pi - \pi^*$ associated with polarity of solvents. The results also revealed that the dyes absorb at the visible region of the electromagnetic spectrum. Again, this explains why the dyes are coloured (Bello, Martin and Obi, 1999).

The FTIR characterization of the dyes revealed the presence of C – O from phenol, C – N and N – H from amines, C – H from alkane, N = O from nitro compounds and – OH from alcohol in the dye 1. The spectrum of dye 2 shows strong absorption bands that reveal the presence of C = C of alkenes, C – O of phenols, C – H of alkanes, N = O of nitro groups, = C – H of aromatic hydrocarbons, N – H of amines and – OH groups of alcohol. The spectrum of dye 3 revealed the presence of = C – H of aromatic hydrocarbons, C – O of phenols, N = O of nitro group, – OH of carboxylic acids, C – H of alkane, – OH of alcohol and N – H of amines. While the spectrum of dye 4 revealed absorption bands of C = C from aromatic hydrocarbons, C – O from phenols, C – N from amines, N = O from nitro groups, – OH from phenols and N – H from amines. The functional groups observed in the dyes conformed to the presence of the chromophoric and the auxochromic groups observed in their structures. (Otutu, Efurhievwe and Ameru, 2014)

Table 3: results of Wash, Heat and Light Fastness on Dyed Wool, Polyester, Nylon and Cotton Fabrics.

Dye	Fabrics	Colour on Fabrics	Fastness Rating		
			Wash fastness	Light fastness	Heat fastness
1	cotton	Tomato 1	4/5	5/5	4/5
	nylon	brown	4/5	5/5	4/5
	polyester	Brown	4/5	5/5	4/5
	Wool	Tomato 3	2/5	5/5	4/5
2	cotton	Cornsilk 3	4/5	5/5	4/5
	Nylon	Cornsilk	4/5	5/5	4/5
	polyester	Cornsilk	4/5	5/5	4/5
	Wool	Cornsilk 2	3/5	5/5	4/5
3	cotton	Yellow	4/5	5/5	4/5

4	Nylon	Yellow	4/5	5/5	4/5
	polyester	Yellow	4/5	5/5	4/5
	Wool	yellow	3/5	5/5	4/5
	Cotton	Golden	4/5	5/5	4/5
	Nylon	Golden	4/5	5/5	4/5
	Polyester	Golden	4/5	5/5	4/5
	Wool	Golden	3/5	5/5	4/5

Table 3 above shows the results of wash, heat and light fastness of the dyes on wool, cotton, nylon and polyester fabrics. The colours of the dyes on the fabrics include golden, brown, yellow, cornsilk and tomato, which show different strengths of colouration on different fabrics. The colour strength of the dyes were more solid on nylon, followed by cotton, wool and then the polyester. The excellent colour strength as shown by nylon was an indication that the nylon has better affinity for the dye molecules which may be due to non-crystalline nature of the nylon fabric which makes it easier for the dye molecules to penetrate into the material.

3.0 Conclusion

From the results of this work, 4 – nitroaniline has shown to have promising potentials in the production of monoazo disperse dyes with excellent colourations and good spectral properties. The dyeing and fastness properties as exhibited by the dyes, shows that the dyes will have great industrial application in the textile industries.

4.0 Acknowledgement

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