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SPECTROPHOTOMETRIC AND INFRA-RED ANALYSES OF AZO REACTIVE DYES DERIVED FROM 2-METHYL-3-(2'-METHYLPHENYL)-6-ARYLAZO-4- OXOQUINAZOLINE

*[1]Adedeji Olumide Adeniyi, [2]D.E.A. Boryo, [3]Istifanus Yarkasuwa Chindo, [4]A.A. Mahmoud

[1]Department of Primary Education, Federal College of Education, Kano
[2]Polymer Unit, Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi
[3]Organic Unit, Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi
[4]Inorganic Unit, Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi

*Corresponding Author Email Address: ginshikijournal@gmail.com

ABSTRACT

Ultraviolet-visible and infrared spectroscopic techniques were used to determine the possible composition and functional groups present in a series of quinazoline based mono azo reactive dyes (DM_{1-5}) which was prepared by coupling 2-methyl-3-(2'-methylphenyl)-6-arylazo-4-oxoquinazoline diazonium solution with five (5) cyanurated coupling components . The result of visible absorption spectra showed that the λ_{mat} obtained for each dye depends on the coupling component used and that the λ_{max} tend to shift to the shorter wavelength (hypsochromic shift) as the auxochromes appear to have influence on the absorption peak of the dyes... The IR spectral showed all the characteristics and representative of azo reactive dyes, with characteristic band in the range of 3400 - 3309 cm^{-1} indicating the presence of -OH and –NH stretching vibration, 1382 - 1049 cm^{-1} for the presence of –C-N, 1141-1010 cm^{-3} for –S=0 and 925 - 56 cm^{-1} for the presence of -C-Cl . The azo band occurred in the region of 1458 - 1411 cm^{-1} which is due to stretching vibration of the -N=N- group. A strong band at 1643 - 1604 cm^{-1} is due to the stretching vibration of -C=O group of the quinazoline compound. However, the IR spectrum did not actually reveal the chemical structure of the reactive dyes being studied. Further studies could be conducted using GCMS and NMR spectroscopy to confirm the structure of the dyes.

Keywords; Quinazoline, Azo reactive dye, UV and IR Spectroscopic Techniques.

INTRODUCTION

Synthetic dyes are extensively used in the textile and printing industries (Moreira *et al*., 2000; Soares *et al*., 2014, Park *et al*., 2016). Azo dyes account for the majority of all textile dyestuffs produced and have been the most commonly used synthetic dyes in the textile, food, paper making, colour paper printing, leather and cosmetic industries (Powell *et al*., 2019, Carthel *et al*., 2015 and Chang *et al*., 2011). They are the largest class of dyes (Stolz, 2021) and have one or more azo groups (R_1–N=N–R_2) having aromatic rings mostly substituted by sulfonate groups. These complex aromatic substituted structures make conjugated system and are responsible for intense colour, high water solubility and resistance to degradation of azo dyes under natural conditions (O'Neill *et al*., 2015, Rajaguru *et al*., 2018).

Azo colourant encompasses azo linkage in their chemical structure and is therefore capable of colouring diverse substances by selective reflection or by transmission of daylight. It ranges in shade from greenish yellow to orange, red and brown (McLean and Freas 2017). The colours depend largely on the physical properties. The part of azo colourant molecule which produces colour, the chromophoric group is a double bonded azo linkage, which alters the colour of a substrate, either by selective absorption or by scattering of visible light (Navarro and Sanz, 2019).

Reactive dyes are a class of highly coloured organic substances, primarily used for tinting textiles that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fibre. The dyestuff thus becomes a part of the fibre and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption (Dermirbas *et al*., 2009).

Monofunctional reactive systems can react with one of the nucleophilic groups in the fibre, examples are halo triazine and vinyl sulphone systems (Patel *et al.,* 2018). Also the dichlorotriazine, difluoropyrimidine and dichloroquinoxaline heterocyclic ring systems, have two equivalent replaceable halogen substituents. However, when one of these halogen atoms is displaced by reaction with functional groups in the fibre or with alkali in the dye bath, the reactivity of the remaining halogen substituent is greatly decreased (Burkinshaw *et al.,* 2016).

Patel *et al.* (2018) noted that in conjugated ring system, colour changes are caused by changes in extent of delocalization of electrons and more delocalization shifts the absorption max to longer wavelengths making the light absorbed redder, while less delocalization shifts the absorption max to shorter wavelengths.

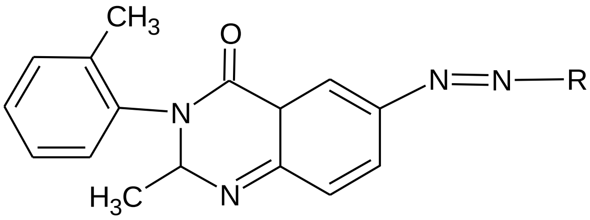
The spectrophotometric analysis, which includes study of absorption max (λmax) and absorption spectrum, gives a rough outline of the chemical structure of commercial dyes, it can help to follow the course of dyeing and dye degradation by the microbial cultures in comparison to the respective controls (Yinon *et al.,* 2014). The Fourier Transform Infrared (FT-IR) spectroscopy is an important physical technique among other techniques such as mass spectrometry, ultraviolet-visible and nuclear magnetic resonance spectroscopy are used in characterization of dye samples. FT-IR spectroscopy is used to study the functional groups present in molecules and for the characterization of covalent bonds within the molecules. FT-IR spectroscopy is a non-destructive, fast and sensitive physical technique for the analysis of organic compounds with minimum sample preparation (Yinon *et al.,* 2014). It can serve as a fingerprint technique for the classification of unknown compounds; therefore it is very helpful in classifying raw materials and ingredients that are used in dyes, paints, polymers, plastics, coatings, laminates, pharmaceuticals, foods and other consumer products. It is also useful for the structural elucidation and confirmation of known and novel natural organic compounds/ products isolated from terrestrial plants and algae with the aid of other physical techniques such as mass spectrometry and NMR spectroscopy (Cole and John 2017).

FT-IR spectroscopy is also used in the analysis of fats and oils and it can also be associated with 'green analytical chemistry' because this technique reduces the use of chemical reagents hazardous to the environment and human health. FT-IR spectroscopy is widely used as a powerful analytical tool in oil and food research to qualitatively and quantitatively analyze specific organic food components in combination with certain chemometric packages (Yinon *et al.,* 2014).

MATERIALS AND METHODS

The dyes selected for this study were a series of quinazoline based mono azo reactive dyes (D_{1-6}) which were prepared by coupling 2-methyl-3-(2'-methylphenyl)-6-arylazo-4-oxoquinazoline diazonium solution with five (5) cyanurated coupling components using standard procedures as established by AATCC Test method, technical manual and standard (2018).

The general structure of the dye is shown below;



Where R = Cyanurated coupling components D_1-D_6.

Structure 1: General structure of the Synthesized dyes

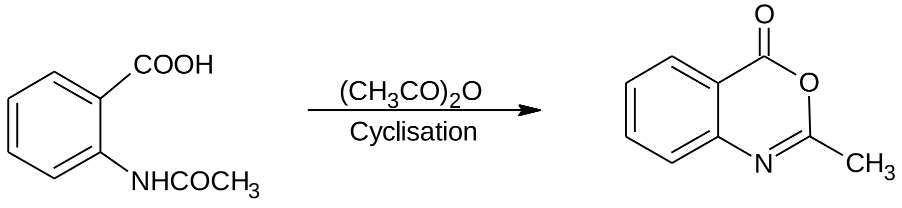
The spectrophotometric properties of the dyes were examined using procedure given by Navarro and Sanz (2019). 0.01 g/dm^{-3} of the dye samples solution were prepared and each solution was then scanned from 400-800 nm by Spectrum Version UV-visible spectrophotometer at NARICT, Zaria. FT-IR analysis of each dye samples was carried out on FTIR-8400S Fourier Transform Spectrophotometer at NARICT Zaria. This is to analyse the synthesized dye samples for functional groups present in the dye molecule

Experimental

The procedures used in the research are standard procedures as established by AATCC Test method, technical manual and standard (2018)

Preparation of 2-methyl-3, 1-benzoxazin-4-one:

A mixture of N-acetyl anthranilic acid (17.9 g, 0.1 mole) and acetic anhydride (36 ml) was refluxed for 30 minutes. The solid which separated on cooling the reaction mixture was filtered and washed thoroughly with dry petroleum other.



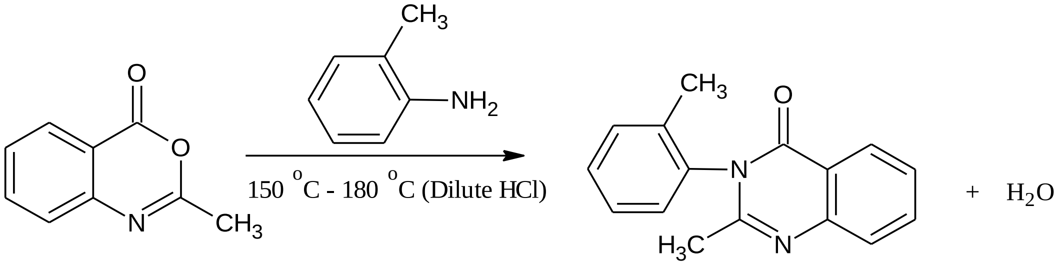
Eqn. 1

N-Acetyl Anthranilic acid

2-methyl-3,1-benzoxazin-4-one

Preparation of 2-methyl-3-(2'-methylphenyl-4-oxoquinazoline)

2-methyl-3,1-benzoxazin-4-one (16.1 g, 0.1 mole) was suspended in o-toludine (10.7 g, 0.1 mole) and heated to 150 – 180 °C for 8-10 hours with vigorous, shaking. The reaction mass was decomposed with dilute hydrochloric acid. The solids separated out were filtered, dried and purified from methanol-water.



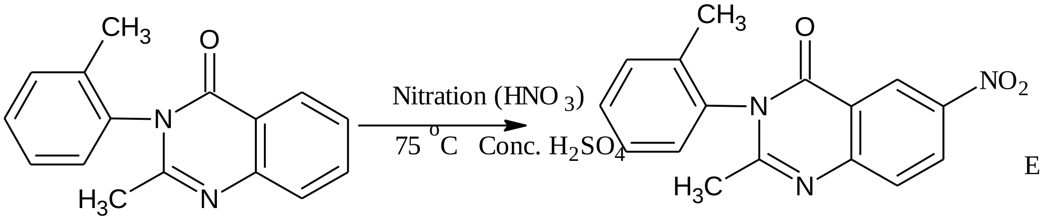
Eqn. 2

2-methyl-3,1-benzoxazin-4-one

2-methyl-3-(2'-methylphenyl)-4-oxoquinazoline

Preparation of 2-methyl-3-(2'methylphenyl)-6-nitro-4-oxoquinazoline

2-methyl-3-(2'-methylphenyl-4-oxoquinazoline) (7.53 g, 0.03 mole) was dissolved in concentrated sulphuric acid (20ml), forming nitric acid (10 ml, sp.gr. 1.5) was then added in one portion keeping temperature below 75 ^{0}C by external cooling. The reaction mixture was poured on ice (200 g) and allowed to stand overnight. Tiny needles separated out of the liquor, it was collected, washed and crystallized from glacial acetic acid in colourless needles.

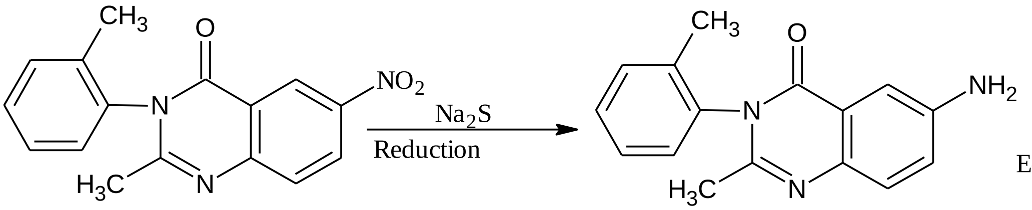


Eqn. 3

2-methyl-3-(2'-methylphenyl)-4-oxoquinazoline 2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline

Preparation of 2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline:

2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline (5.92 g, 0.02 mole) was suspended in a solution of sodium sulphide (14.4 g, 0.06 mole) in water (75 ml) was refluxed for 2 hours, yielding a deep reddish brown solution after cooling and diluting with water (75 ml) and strongly acidifying with hydrochloric acid, the solution was boiled for 20 minutes and filtered. Addition of sodium carbonate precipitated free amines as pale yellow compound. The product was crystallized from ethanol.

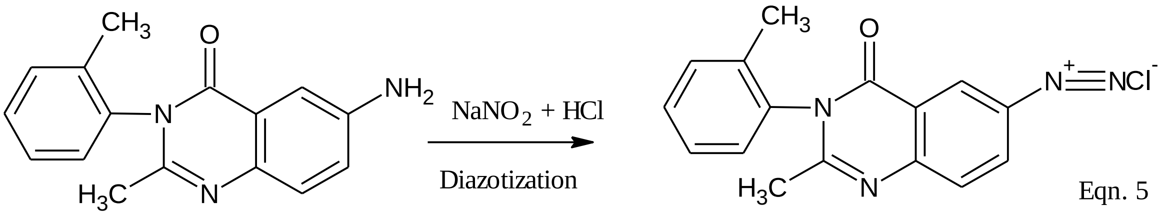


Eqn. 4

2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline 2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline

Formation of diazonium chloride of 2-methyl-3-(2'-methylpheny)-6-amino-4-oxoquinazoline (Diazo solution A]

2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline (2.66g, 0.01 mole) was suspended in water (60 ml). Hydrochloric acid (86 g, 0.024 mole) was added drop wise to this well stirred suspension. The mixture was gradually heated to 70 ^{0}C till clear solution obtained. The solution was cooled to 0-5 ^{0}C in an ice bath. A solution of $NaNO_2$ (0.6 g) in H_2O (4 ml) previously cooled to 0 ^{0}C was then added over a period of 5-minute with stirring and maintaining temperature at 0 -5 ^{0}C, stirring was continued for 1hour maintaining the same temperature with positive test for nitrous acid on starch paper. After destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear diazo solution at 0 - 5 ^{0}C was used for subsequent coupling reactions.

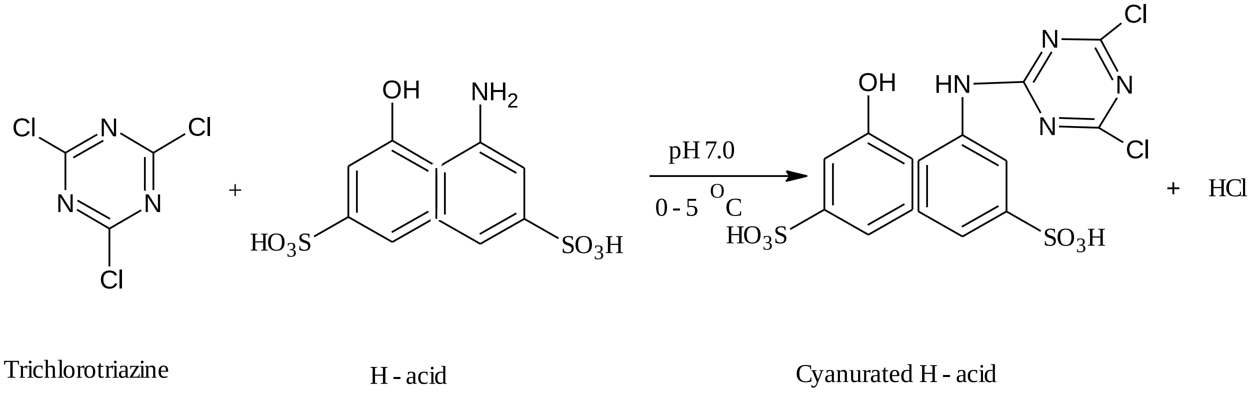


Eqn. 5

2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline Diazonium solution

Preparation of Coupling Components

A total of six coupling components were used in this research. The coupling components (DM_1-DM_6)) were treated with Trichlorotriazine (2.0 g) Eqn. 6.



Formation of cyanurated coupling component-- Equation 6

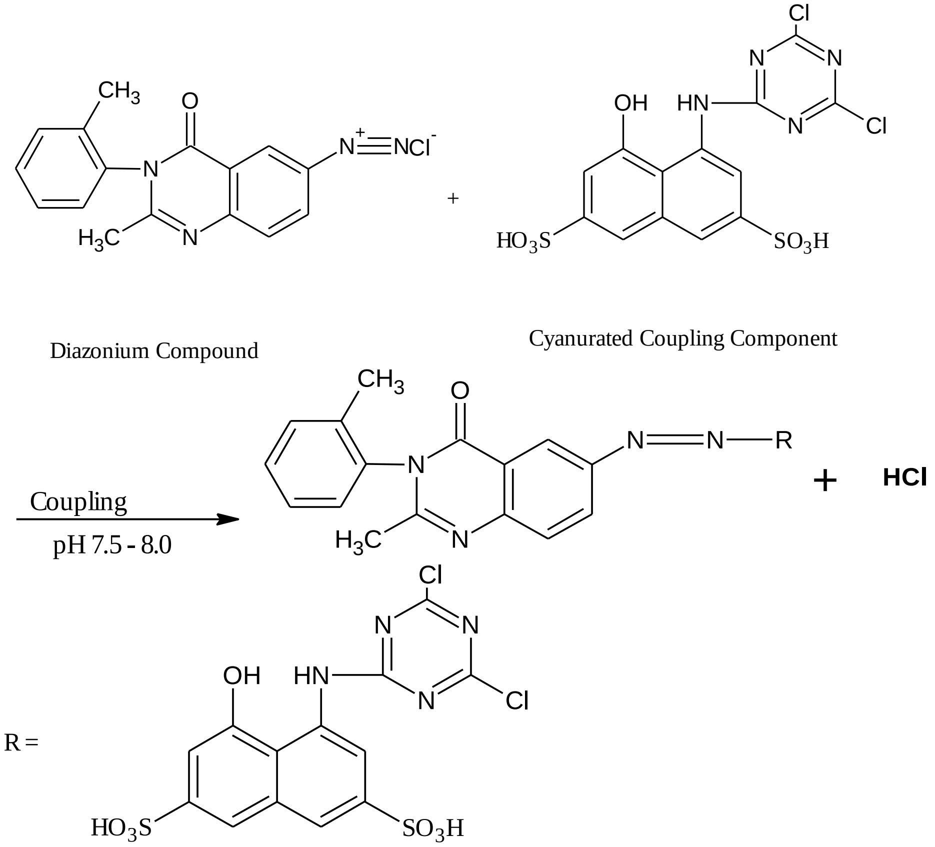
Table 1: Coupling Components

Dye No.	Coupling Components	Molecular Formula	Mol. Weight
DM1	H-acid	$C_{26}H_{20}O_8N_5S_2Na_2$	616
DM2	J-acid	$C_{26}H_{21}O_5N_5SNa$	526
DM3	K-acid	$C_{26}H_{20}O_8N_5S_2Na_2$	616
DM4	Tobias acid	$C_{26}H_{22}ON_5$	420
DM5	N-phenyl J-acid	$C_{32}H_{25}O_5N_5SNa$	602

Coupling Reactions

Mono-functional Reactive Dye

Cyanurated H-acid (3.19 g, 0.01 moles) was suspended in water (20 ml) and cooled below 5 ^{0}C in an ice bath. The diazoniun solution was then be added in drops over a 10 - 15 minutes period maintaining the pH 7.5 - 8.0 by simultaneously addition of sodium carbonate solution (10 % w/v) The reaction mixture was continuously stared for between 2 - 3 hours and heated up to 60 ^{0}C, solution of sodium chloride (5 % w/v)was then added until coloured precipitate was obtained. The precipitate was filtered and washed with small amount of dilute sodium chloride, the solid was dried at 80 - 90 ^{0}C and extracted with DMF. A purple dye was precipitated by diluting the DMF extract with excess chloroform, the dye was then filtered, washed and dried at 60 ^{0}C. .This was repeated for all the other coupling components (Patel *et al.,* 2018). Eqn. 8



Coupling Reaction of Mono-functional Reactive Dye (DM_1-DM_6) – Equation 8

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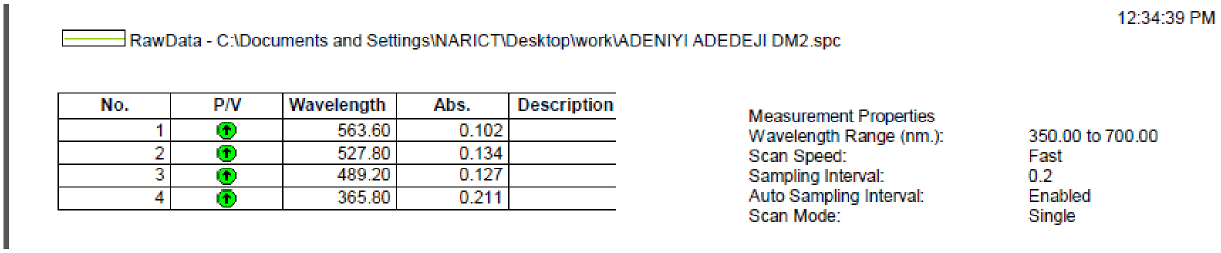
RESULTS AND DISCUSSION

The results of the UV-VIS spectroscopy of DM 2 is presented in Table 1 and Figure 1. Tables 2 shows the colour and the spectroscopic properties of the dyes (D $_{1-5}$)..

Table 1 UV-Visible Spectral Scan of DM 2



RawData - C:\Documents and Settings\NARICT\Desktop\work\ADENIYI ADEDEJI DM2.spc

12:34:39 PM

No.	P/V	Wavelength	Abs.	Description
1	↑	563.60	0.102	
2	↑	527.80	0.134	
3	↑	489.20	0.127	
4	↑	365.80	0.211	

Measurement Properties	
Wavelength Range (nm.):	350.00 to 700.00
Scan Speed:	Fast
Sampling Interval:	0.2
Auto Sampling Interval:	Enabled
Scan Mode:	Single

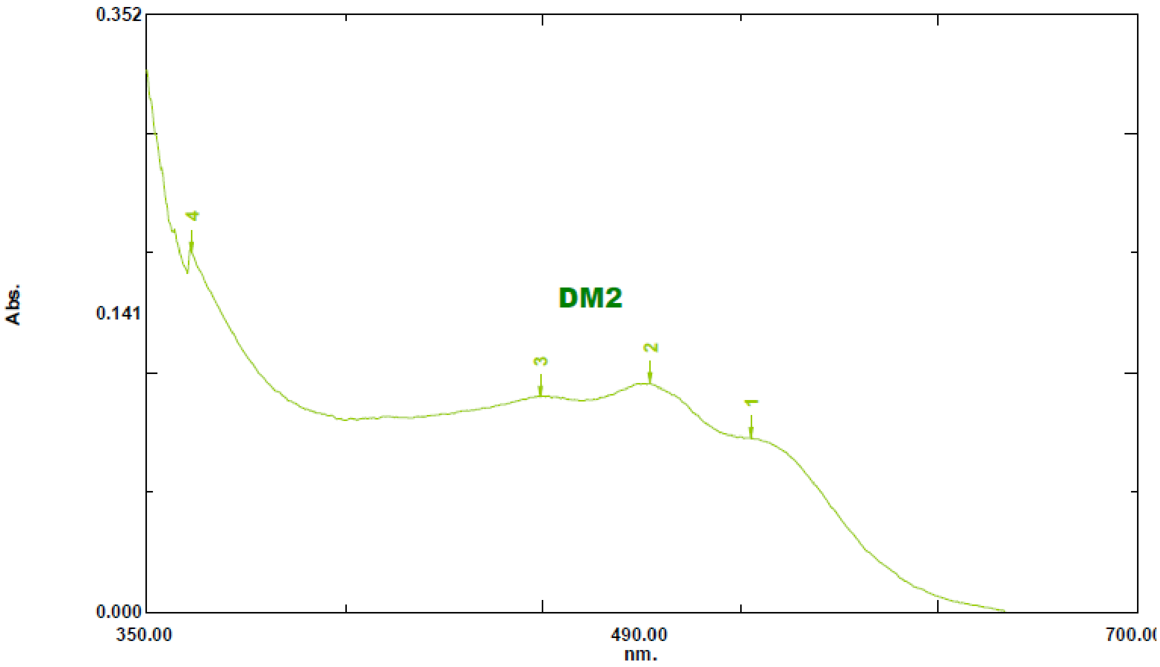
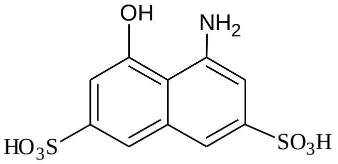


Figure 1: UV-Visible Spectral Scasn of DM 2

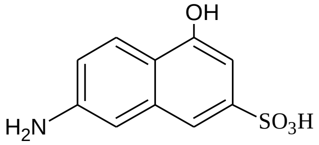
Table 2 UV-VIS. Spectroscopic Properties of Mono-functional Reactive Dyes

Dye No.	λ_{max} (mm) in water	Absorbance (optical density)	Cone in dm^{3}mol^{-1}	Colour of Dye
DM$_1$	586	0.418	1.96 x 10^{-5}	Dark Blue
DM$_2$	527	0.134	2.11 x 10^{-5}	Reddish Brown
DM$_3$	479	0.580	1.62 x 10^{-5}	Yellow
DM$_4$	396	0.460	1.96 x 10^{-5}	Brown
DM$_5$	412	0.087	1.66 × 10^{-5}	Brown

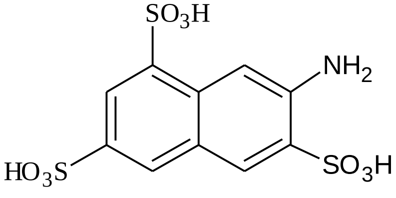
It is apparent that the values of the λmax depend on the coupling component used, The results showed that the λ_{max} tends to shift to the shorter wavelength (hypsochromic shift), the functional groups attached to the dye (auxochrome) and its arrangement appear to have influence on the absorption peak of this dye which tend to appear at the shorter wavelength (blue shift). The colour observed for each dye with reference to Table 1 is due to the transition of electrons and the presence of additional substituents this is agreement with Jooneck *et al.,* 2017 and Patel *et al.,* 2019. The structures of the six coupling components are given below



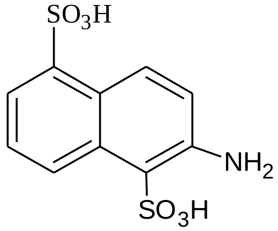
H - acid (1)



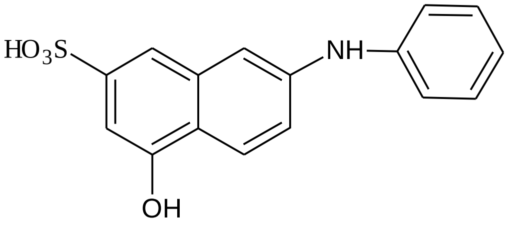
J - acid (2)



K - acid (3)



Tobias acid (4)

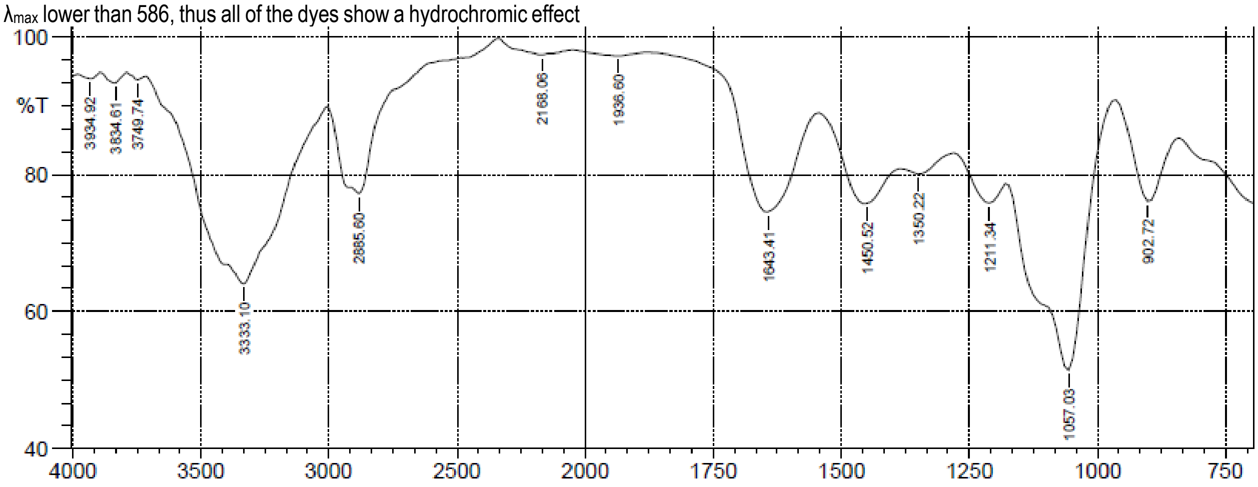


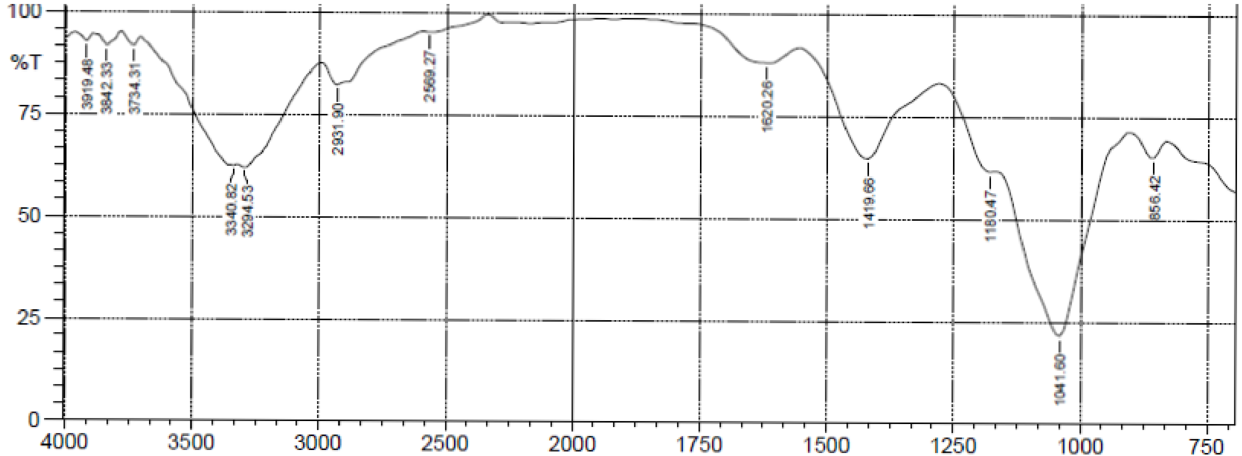
N -Phenyl J acid (5)

In DM_1 (1) there are more places for transition of electrons and the presence of both –OH and –NH_2 groups hence λmax 586. In DM_2 (2), DM_3 (3) and DM_5 (5) slightly lower effect is produced due to the lower number of electrons and the transition is fast, therefore λ_{max} 527, 479, 412 is lower than DM_1 586 (1). The same effect is also shown in dyes DM_4 (4). While for dyes DM_3 (3) the substituent are similar as in DM_1 (1) but the transition of electrons is fast due to the vicinity of –NH_2 and –SO_3H groups which caused neutralization of electrons (amine and suphonic acid group) to take place and hence λ_{max} lower than 586, thus all of the dyes show a hydrochromic effect due to the –OH group with respect to DM_1 (1). Also the π cloud of electrons over the entire length of the structure in DM_1 lowers the energy for light absorption thus higher lambda max This result is similar to what Jooneck *et al.,* 2017 and Patel *et al.*, 2019 found in a similar study conducted on azo dye Orange-3R/Orange-16.

FT-IR Spectroscopic Properties of the synthesized dyes

The results of the FT-IR of the synthesized dyes are presented in Table 3. The IR spectra depicts characteristic of azo dyes showing peaks corresponding to the functional groups present in the synthesized dyes. While Figure 2 is the FTIR spectra of D 1 - 5

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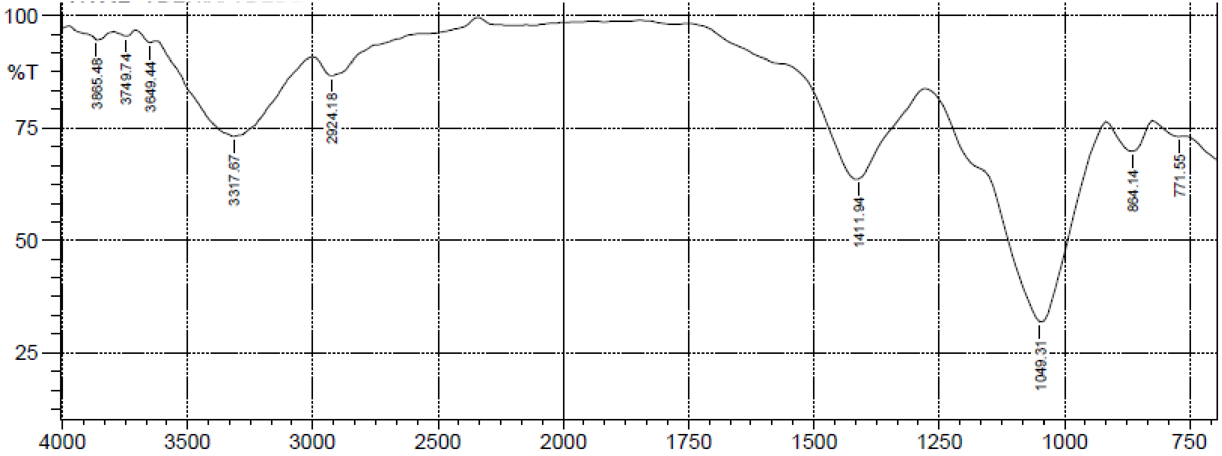
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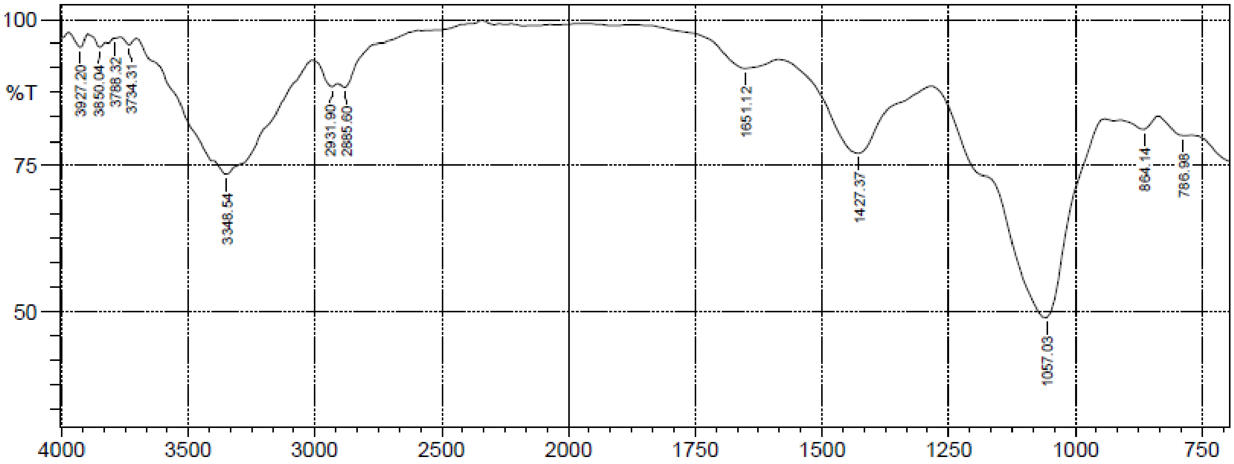
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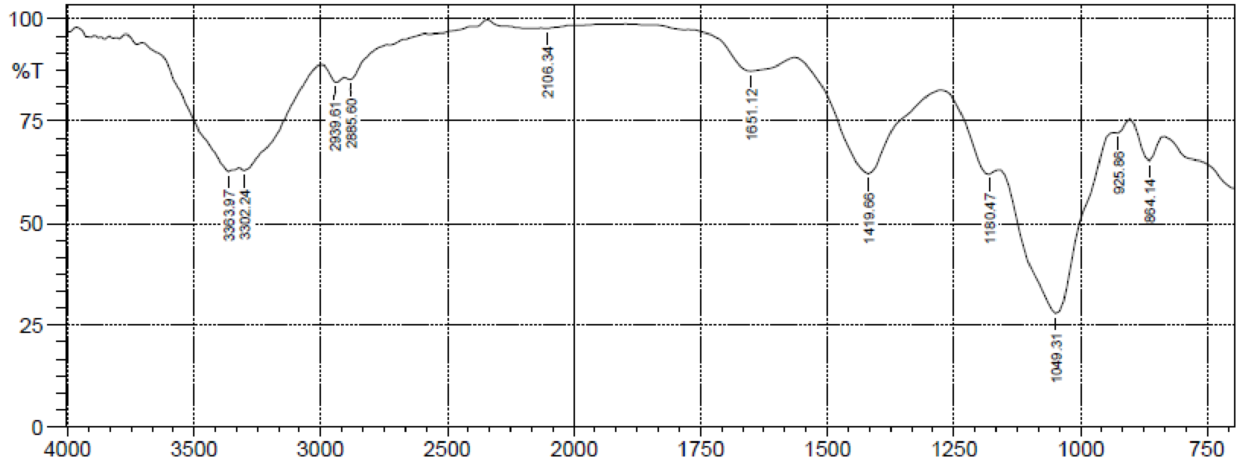

Figure 2: FTIR Spectra of the Dyes (DM 1 – 5)

Table 3: FT-IR Spectra of Mono-functional Reactive Dyes

Dyes	IR (cm^{1})
DM1	3333 (-OH & -NH), 1643 (-C=O), 1450 (-N=N-), 1350 (C-N), 1057 (-S=O), 902 (C-CI).
DM2	3340-3294 (-OH & -NH), 1620 (-C=O), 1418 (-N=N-), 1385 (C-N), 1041 (-S=O), 856 (C-CI)
DM3	3317 (-OH & -NH), 1653 (-C=O), 1411 (-N=N-)1382 (C-N), 1049 (-S=O) 864 (C-CI).
DM4	3348 (-OH & -NH), 1651 (-C=O), 1427 (-N=N-) 1390 (C-N), 1057, (-S=O), 864 (C-CI).
DM5	3363-3302 (-OH &-NH), 1651 (-C=O), 1419 (-N=N-) 1395 (C-N), 1049(-S=O), 864 C-CI).

The IR of all the dyes showed the characteristic band in the range of 3400 - 3309 cm^{-1}. This indicates the presence of O-H and N-H stretching vibrations. The azo (-N=N-) band occurred in the region of 1458 – 1411 cm^{-1} which is stretching vibration of azo group. A strong band at 1643 – 1604 cm^{-1}is due to the stretching vibration of carbonyl (C=O) group of the quinazoline compound and absorption band at 1350 – 1180 cm^{-1} is due to the C-N stretching vibration. The band at 1057 – 1041 cm^{-1} is due to the stretching vibration S=O group, while the band at 856 – 700 cm^{-1}is due to the stretching vibration of C-Cl group.

The IR values obtained are similar to the functional groups reported by Divyesh *et al.* (2011). In the synthesis and characterization of reactive dyes based on 2-phenyl-3-[4-aminophenylsulphonamido]-quinazoline-6-sulphonic acid and of Colthup *et al* (2021) and Bassler *et al.* (2018) in determining functional groups of commercially available Ink-Jet printing reactive dyes using IR spectroscopy. In general the IR spectra of all the dyes showed the characteristic band in the range 3675 - 3500 cm^{-1} indicating the presence of OH and NH stretching vibration in addition to absorption band at 1520 – 1506 cm^{-1} is due to NH bending vibration. The band appearing at 1440 – 1415 cm^{-1} is due to the stretching vibration of azo (-N=N-) group. A strong band at 1670 – 1650 cm^{-3} is due to stretching vibration of the carbonyl (-C=O) group of the quinazoline molecule and absorption band 1395 – 1380 cm^{-1} is due to the C-N stretching vibration. The band at 1345 – 1040 cm^{-1} is due to stretching vibration of S=O group while the band at 1325 – 1310 cm^{-1} is due to bending vibration of O–H group and the C–Cl stretching vibration appeared at 770 - 760 cm^{-1}. Also Patel *et al.* (2019) in research synthesis and characterization of reactive dyes based on 2-phenyl-3-(3,4 aminophenylsulphomido)-quinazolinone-6-sulphonic acid, reported characteristic band in the range 3630 - 3510 cm^{-1} indicating the presence of OH and NH stretching vibration in addition to absorption band at 1655 cm^{-1} is due to (-C=O) of the quinazoline molecule. The band appearing at 1430 cm^{-1} is due to the stretching vibration of azo (-N=N-) group. A strong band at 1380 cm^{-3} is due to stretching vibration of the (-C-N) group bending vibration and the band at 1320 – 1166 cm^{-1} is due to stretching vibration of -S=O group. While the band at 762 cm^{-1} is due to bending vibration of the C–Cl stretching vibration.

Conclusion

The experimental results showed that the λ_{mat} obtained for each dye depends on the coupling component used and a range of colours was obtained by changing the positions of auxochromes in the heterocyclic ring system. The IR spectra depicts characteristics of azo dyes having showed peaks corresponding to the functional groups present in a typical azo dye such as the chromophore (–N=N-) and auxochromes (O-H, -NH, C=O, C-N, S=O and –Cl). However, the IR spectrum did not actually reveal the chemical structure of the reactive dyes being studied, but the IR spectral obtained from this study could be compared with the dye databases which contain the IR spectral of reactive dyes with known chemical structure and compositions.

Recommendation

Activity in the area of synthesis of new colourant is fluid and dynamic therefore it is necessary to continue further work until auxochromes of desired properties is obtained

Also the use of GCMS and N.M.R spectroscopy could as well be undertaken to further confirm the dyes chemical structure.

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