Nigerian Research Journal of Chemical Sciences **(ISSN: 2682-6054)**
Volume 8, Issue 1, 2020

SYNTHESIS, CHARACTERISATION AND PHYSIOCHEMICAL PROPERTIES OF REACTIVE DYES

Iyun, O. R. A., Rofiat, A. O., *Titus, M. R.
Department of Chemistry, Ahmadu Bello University, Zaria, Kaduna State, Nigeria
*Corresponding author: meetmotitus@gmail.com

ABSTRACT

Four new reactive dyes were synthesized by coupling a cyanurated-H-acid (8-amino-1-naphtol-3,6-disulphonic acid monosodium salt) with some coupling components (thiophene-1-dioxide, thiophene-2-carboxaldehyde, thiophene-3-carboxamine and dimethyl aminobenzyldehyde). The synthesized dyes had percent yield, 58.8% - 62.5% and were characterized by determining their melting points (212 to 323.8 °C). They were soluble in a range of solvents including water, diethyl ether, DMF and acidified ethanol (0.15%) and acetone. The functional groups were detected using the FTIR with –N=N stretch at 1490.4 to 1520 cm^{-1}, -NH stretch at 3302-3373 cm^{-1} and a -C=C stretch at about 801.25-1625cm^{-1} for the dyes respectively. The synthesized dyes absorbed at the UV-Vis region of the electromagnetic spectrum with a maximum absorption wavelength (λ_{max} (nm)) of 413 nm - 565 nm. The dyes were applied on different particle sizes of the pulverized plum seeds and their percentage (%) exhaustion was determined as 52.16% - 93.98% for all the dyes and 0.4 mm particle size absorbed the most.

Abbreviations: DMF (dimethylformamide), IR (infrared), UV-VIS (ultraviolet-visible)

Key words: Coupling, cyanurated-H-acid, exhaustion**, r**eactive dyes, thiophene

INTRODUCTION

One of the major problems facing the dyer from time has been the production of coloured fabrics possessing good fastness properties. This involves attaching a dye molecule to a fibre substance in such a way that it cannot be easily removed. Reactive dyes are dyes capable of reacting chemically with a substrate to form a covalent dye substrate linkage. The dye molecule forms covalent bonds with the terminal –OH (hydroxyl) group of cellulosic fibres and the terminal –NH_2 (amino) group of polyamide of wool fibres [1-4]. It is expected that the covalent attachment of the dye molecules to the substrate will yield very high wash fastness because covalent bonds are the strongest known binding forces between molecules [5, 6]. The energy required to break this bond must equal the same order as that required to break covalent bonds in the substrate itself [7, 8]. Important properties of these reactive dyes include: excellent wet fastness, brilliant shades and simple application techniques [9, 10].

The structural development of new reactive dyes have been a subject of interest and many novel structures are useful in commercial application to wool, silk and cotton as well their blend with other fibres [11]. These reactive dyes are efficient and also have a skin-deep ease of washing out of the non-fixed portion which happens to be a requirement of dyeing, high reactivity, good yield and also high degree of fixing in particular dyeing [12].

In recent times, reactive dyes have become an inevitable part of not only the textile industries but also for polymeric materials and are used in other areas such as reprographic technology, lasers, functional dye applications, photodynamic therapy, and nonlinear optical systems [13], hence the motivation for continuous research and making of more effective novel reactive dyes with high brilliance, ease of application and good fastness properties. This work describes the synthesis of novel and simple reactive dyes by coupling a cyanurated-H-acid (8-amino-1-naphtol-3,6-disulphonic acid monosodium salt) with some coupling components (thiophene-1-dioxide, thiophene-2-carboxaldehyde, thiophene-3-carboxamine and dimethyl aminobenzyldehyde). The dyes synthesized were characterised by their spectrophotochemical data and applied on pulverised plum seeds of different particle sizes.

MATERIALS AND METHOD

Plum seeds and chemicals

The plum seeds were collected, dried, washed with a bleaching agent to remove the yellow colouration, dried again, pulverized and sieved into different particle sizes (0.4, 0.8, 1.2 and 1.6mm).

All the chemicals used for this study were of the analytical grade unless stated otherwise. Both the 2,4,6-trichloro-1,3,5-triazine, H-acid and coupling components were received from Sigma Aldrich.

Preparation of dyes A-D

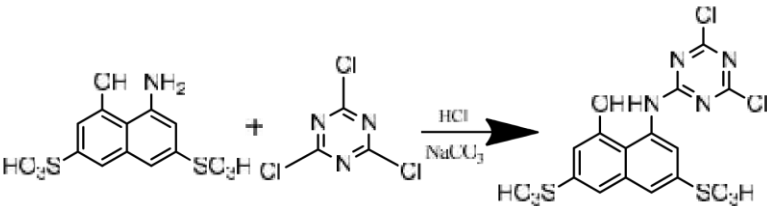
The synthesis of azo reactive dyes requires two organic compounds- a diazonium salt and a coupling components. The diazonium salts reacts as an electrophile with electron- rich coupling component through an electrophilic aromatic substitution mechanism.

Diazotization of the diazo component

Sodium nitrite ($NaNO_2$) (0.83g, 0.01mol) was added to 2.5 ml concentrated sulphuric acid at 30ºC with heating and stirring the mixture to 60-65ºC forover 15 minutes. The temperature was maintained for 30 minutes to ensure complete dissolution of sodium nitrite. The reaction mixture was cooled to 0ºC and 2.5ml of concentrated acetic acid was added with continuous stirring for 10 minutes. The mixture was cooled to 0ºC, and 0.01mol of the diazo component (5amino-4-cyano-N-(2,4-dimethylphenyl)2-methylthiophene-3-carboxamide, dimethylaminobenzaldehyde, 5-aminoN-(4-chlorophenyl)-4-cyano-2methylthiophene-3-carboxamide, Methyl-2-amino-4-((2,4dimethylphenyl)carbonyl)-5methylthiophene-3-carboxylate) was added over a period of 30 minutes and then stirred for another 40 minutes.

Cyanuration of 8-amino-1-naphtol-3,6-disulphonic acid disodium salt

Cyanuric acid (1.84g, 0.01mol), was stirred in acetone (25ml) at a temperature below 5ºC for a period of one hour. A neutral solution of H-acid (3.19g, 0.01mol) in aqueous sodium carbonate solution (10%w/v) was then added in small lots for about one hour. The pH was maintained neutral by the simultaneous addition of sodium carbonate solution (1%w/v).The reaction was stirred at 0-5ºC for further 2 hours. The product was then used for coupling immediately.

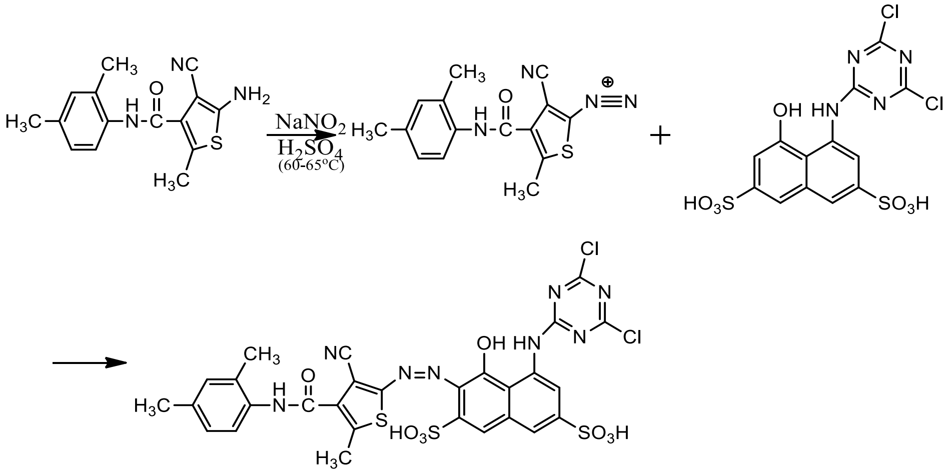


Scheme 1: Cyanuration of H-acid (cyanuric-H-acid with different disazo component)

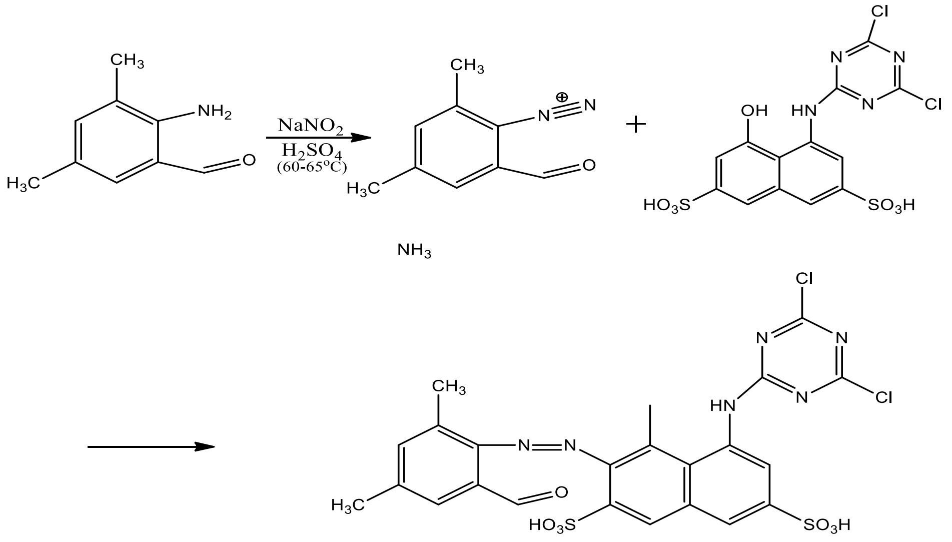
Coupling of diazotized diazo components with cyanurated H-acid

Freshly prepared diazonium salt (0.01mol) was added drop wise to the well stirred solution of cyanurated H-acid (0.01mol). The pH 9 was maintained by the addition of 20% (w/v) Na_2Co_3 with continuous stirring for two hours at 0ºC. The dye was isolated by salting out solution using NaCl, the pH was adjusted to 7 using 5% HCl with continuous stirring for one hour. The reaction mixture was filtered and the precipitated dye collected. The precipitate was washed with 5% (w/v) NaCl solution. The crude dye was dissolved in DMF and ethylacetate was added to precipitate the dye. The precipitate was collected and washed with ethylacetate.

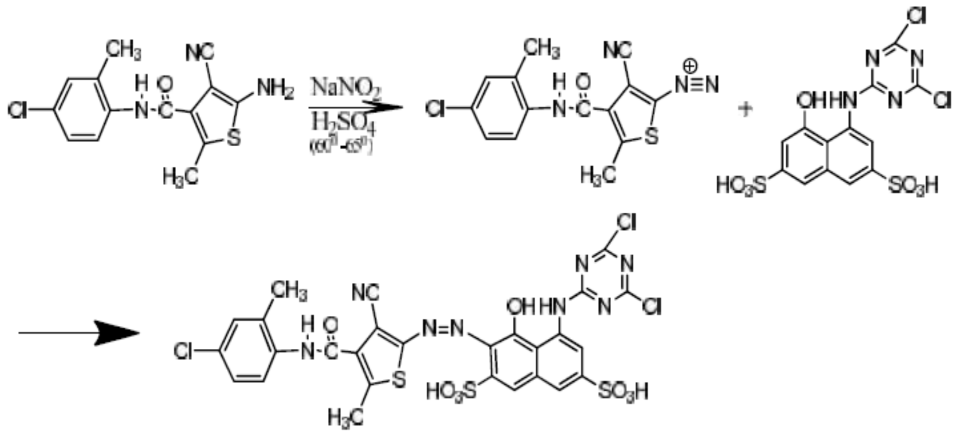
DYE A



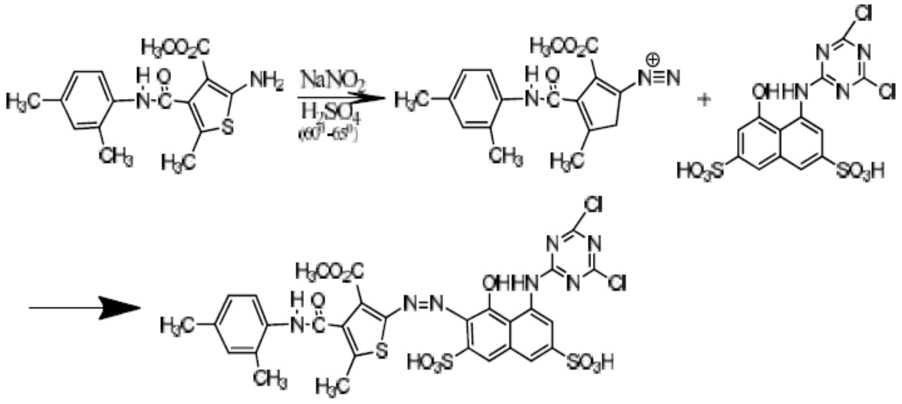
DYE B



DYE C



DYE D



Scheme 2: The reaction schemes of the synthesized dyes A-D

Characterization of the synthetic dyes

The products were characterized by melting point apparatus (Model number: MPAHLSCEA by BEXCO) for melting point determination, molecular mass determination and spectroscopic techniques (FT-IR model: CARY 630 and UV Vis model: CARY 300, both by Agilent Technologies), solubility testing in a range of solvents including water, diethylether, dimethylformamide, ethanol and acetone.

Applications of the synthesized dyes on pulverized plum seeds

A 2% stock solution was prepared for each of the dyes by diluting 2 g of each of the dyes in 100ml distilled water. 1g of the pulverized plum seed of various particle sizes were placed in 50ml dye solution of the synthesized dyes A-D respectively and heated in a water bath for 4hours. Dyeing was carried out utilizing exhaustion technique [14]. The % exhaustion calculated as shown in the formula below;

$$\%\ \text{exhaustion} = \frac{\text{initial absorbance} - \text{final absorbance}}{\text{Initial absorbance}} \times 100\%$$

RESULTS AND DISCUSSION

The structure, %yield, melting point, molecular mass and R_f values of the synthesized dyes are shown in Table 1 while the maximum absorption wavelength (λmax nm)in various solvents including water is shown in Table 2 and the effect of particle size on dye exhaustion shown in Table 3.

The dyes were all very soluble in water, with dye A giving a light purple colour; dye B: yellow; dye C: dark blue, and dye D gave a brown coloration.

The wavelengths of maximum absorbance of the synthesized dyes were determined in water (because it was the most suitable solvent having the highest percentage of solubility) and the other solvents, diethyl ether, ethanol, HCl and acetone, using a UV-Visible spectrophotometer. All the dyes were either sparingly soluble or very soluble in these solvents. The extinction co-efficient (ε) was calculated using the formula $A = \varepsilon CL$ and shown in Table 2

The synthesized dyes applied to different particle sizes of the pulverised plum seeds at 2% shade showed good to excellent dyeing properties especially on the 0.4 mm particle size. The fixation of the dyes on the respective particle sizes reduces with increasing particle size. This is attributed partly to the chemical bond formation of the dye with the substrate (pulverized plum seeds) and also because smaller particles have more pores to hold the dyes based on the principle that small particle sizes have larger surface area [15]. The high melting temperatures means these dyes can be used for high temperature application.

Scheme 1 shows the cynanuration of H-acid, and Scheme 2, the synthesis of the reactive dyes A-D. Figures 1-3 are the Effects of particle size on dye exhaustion. Table 1 is showing the structure and physical properties of the synthesized dyes, while Table 2 shows the UV-Visible data of the synthesized dyes and Table 3 shows the effect of particle size on dye exhaustion while Table 4, infrared absorption bands for the dyes.

A melting point 212-323.8 ºC as shown in Table 1 means that the dyes can be used for high temperature application. Dyes A and B have relatively close R_f values. It could be because of somewhat similar structure of the two molecules. R_f values have often been used to confirm purity of unknown compounds [16].

Table 1: Structure and physical properties of the synthesized dyes

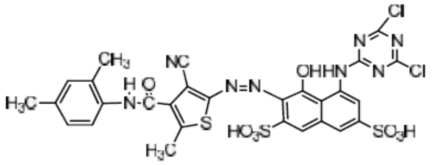
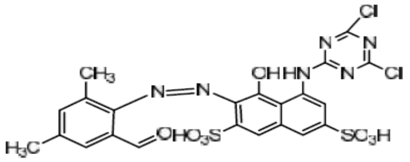
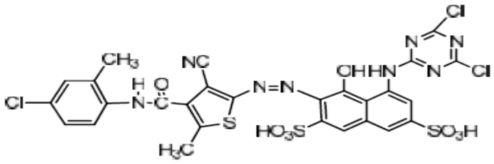
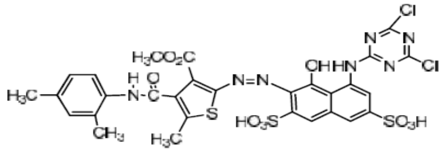
Dyes	**Name and Structure**	**Melting point (ºC)**	**% yield**	**R_f Value**	**Molecular Weight**
A	 (E)-3-((3-cyano-4-((2,4-dimethylphenyl)carbamoyl)-5-methylthiophen-2-yl)diazenyl)-5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthalene-2,7-disulfonic acid	251-254	61.9	0.59	776
B	 (E)-5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-3-((2-formyl-4,6-dimethylphenyl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid	321.4-323.8	56.8	0.56	616
C	 (E)-3-((3-cyano-4-((2,4-dimethylphenyl)carbamoyl)-5-methylthiophen-2-yl)diazenyl)-5-((4,6-	307-309	62.5	0.71	704

Table 2: UV-VIS Data of the synthesized dyes

	dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthalene-2,7-disulfonic acid				
D	 (E)-5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-3-((4-((2,4-dimethylphenyl)carbamoyl)-3-(methoxycarbonyl)-5-methylthiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid	212-214	60.5	0.68	793

DYES	Maximum Absorption Wavelength λ_{max} (nm)					Extinction co-efficient ε (liter/mol/cm)
	Water	**Diethyl ether**	**DMF**	**Ethanol + HCl**	**Acetone**	
Dye A	552	552	552	552	510	42791
Dye B	413	465	400	465	566	34724
Dye C	565	565	565	565	542	39789
Dye D	545	420	545	545	520	43254

Table 3: Effects of Particle Size on Dye Exhaustion

Serial NO	%EXHAUSTION				
	Particle Size	**SAMPLES (DYES)**			
		A	**B**	**C**	**D**
1	0.4mm	93.98%	85.58%	72.58%	54.16%
2	0.8mm	49.35%	82.55%	70.33%	54.47%
3	1.2mm	20.48%	76.68%	52.48%	44.29%
4	1.6mm	7.71%	43.02%	52.61%	32.43%

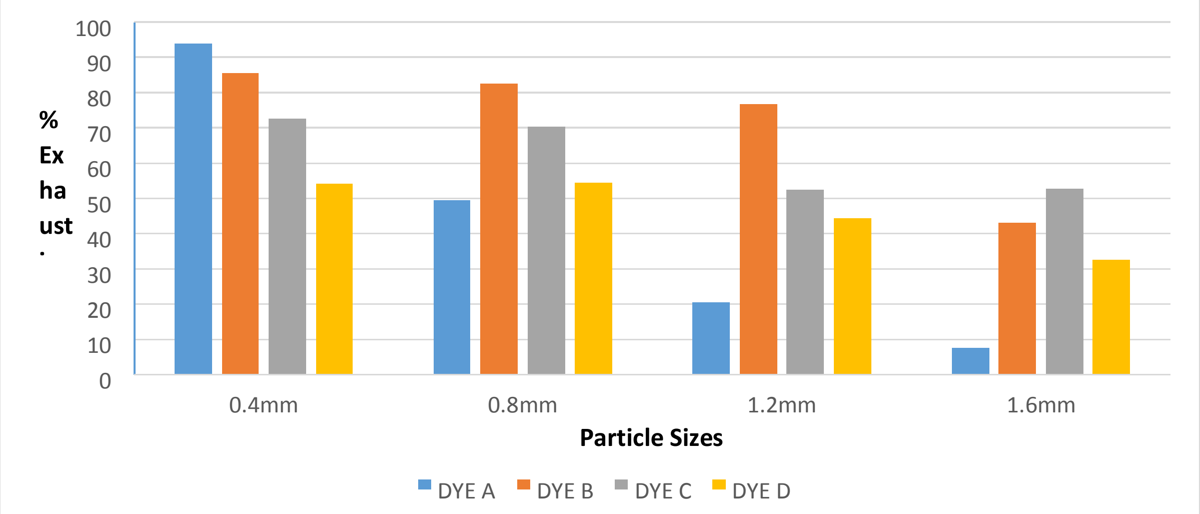


Figure 1: Effects of Particle Size on Dye Exhaustion (a)

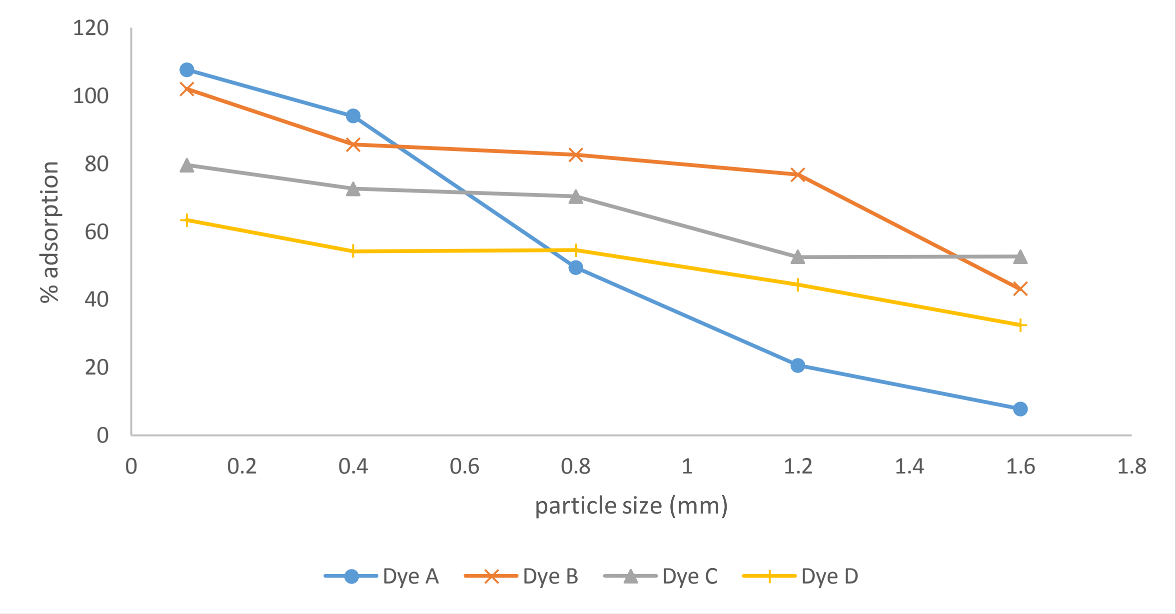


Figure 2: Effect of Particle Size on % Dye Absorption (b)

Table 3, Figures 1 and 2 explain the effect of particle size on the exhaustion of these synthesized dyes. From the trend displayed for the respective dyes A-D, the dye absorption increases with decreasing particle size since at a larger particle size the surface area for absorption per unit volume decreases [16]. This thus explains the decreased % exhaustion of the dyes A-B as particle size increases.

The Infra-Red Spectra of the Dyes

The infrared spectroscopy is one efficient technique used for the characterization of organic compounds, IR spectrophotometers as FT-IR (using CARY 630 FT-IR Spectrophotometer by Agilent Technologies) which was used showed absorption –N=N stretch at 1490.4-1520cm^{-1}, -NH stretch at 3302-3373 cm^{-1} and a -C=C stretch at about 801.25-1625cm^{-1} as further shown in Table 4 below (IR spectra in Figures 3-6).

Table 4**:** Infrared Absorption Band for the Synthesized Dyes A-D

Bands Causing Absorption	**Dye A**	**Dye B**	**Dye C**	**Dye D**
-OH stretching		3511	3528	3351
-C-H stretching	2978	2985	3298	3030
-C-N stretch	1100	1100	1145	1021
-NH stretch	3310	3589	3300	3351
-C=O stretch	1715	1800	1684	
-C=N stretch	1675	1625	1651	1520
-C=C in aromatic ring	1808	1408	1400	1499
-SO_2	1219	1114	1125	1121
-C≡N		2202	2203	2113
Solubility in Water	Very soluble	Very soluble	Very soluble	Very soluble
Colour in Water	Light purple	Yellow	Dark blue	Brown

CONCLUSION

Reactive dyes A-D were synthesized with a very good yield. The synthesized azo reactive dyes which has cyanuric chloride as it reactive component showed excellent dying properties on the substrate (pulverized plum seeds). This is particularly due to the reactivity of the dye and chemical bond formation between the dye molecule and the hydroxyl group of the substrate, also the particle (0.4mm) size aided it fixation

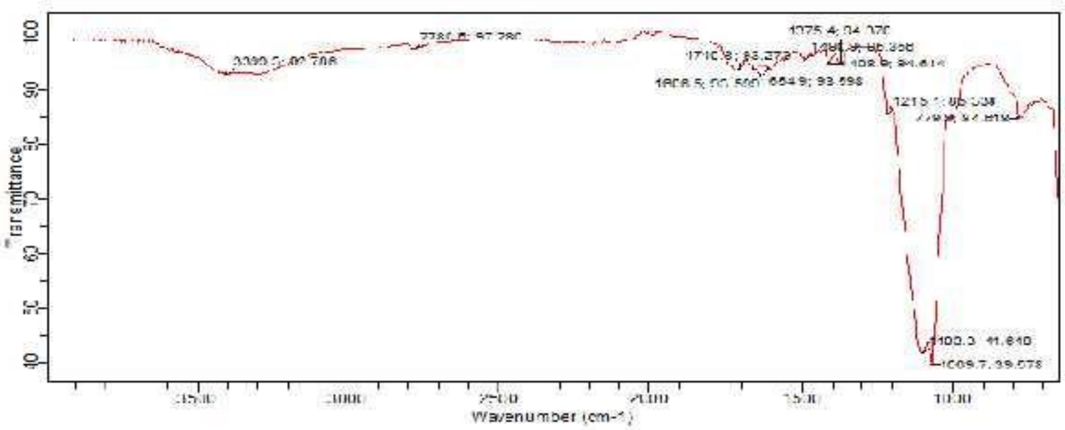


Figure 3: FT-IR Spectrum for Dye A

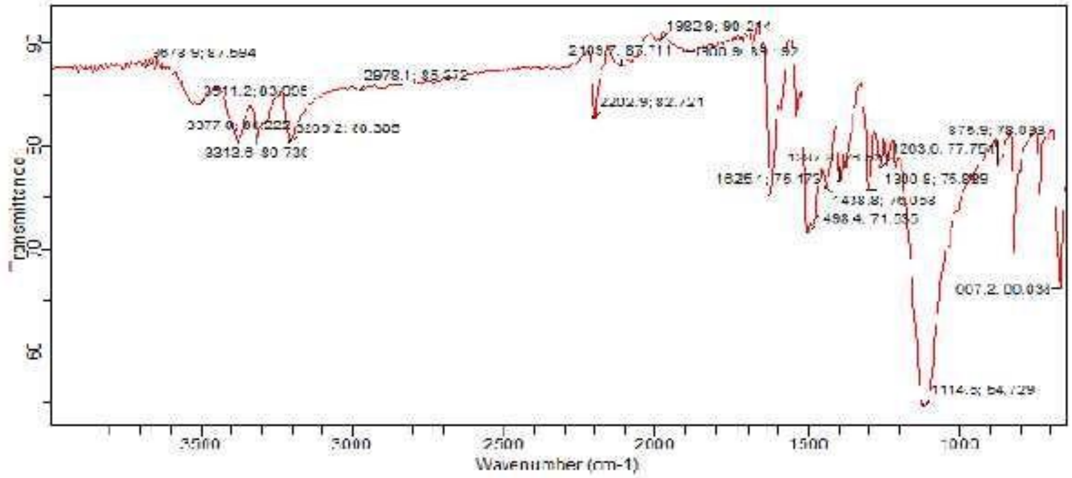


Figure 4: FT-IR Spectrum for Dye B

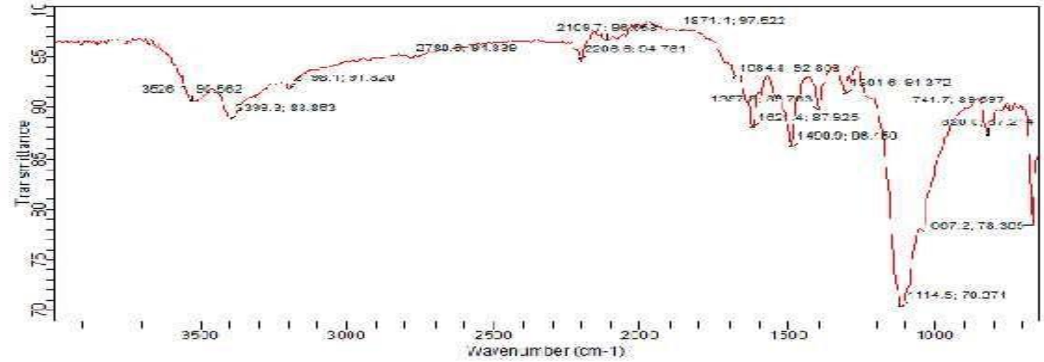


Figure 5: FT-IR Spectrum for Dye C

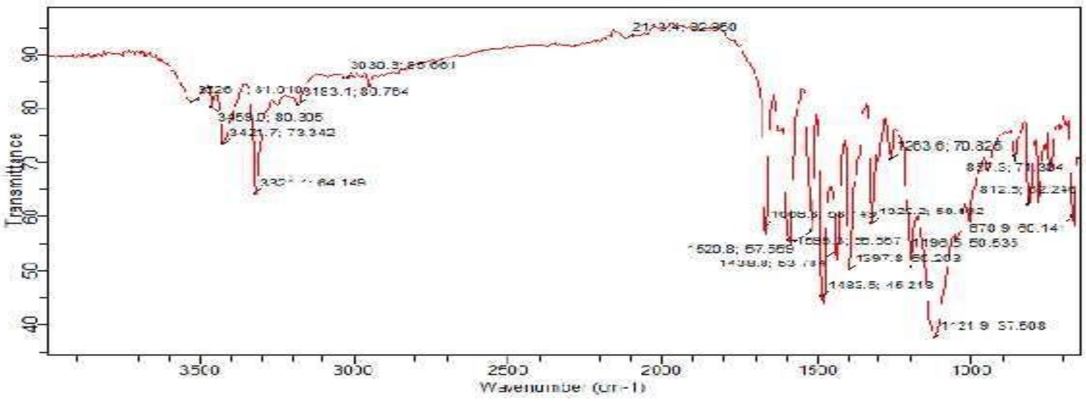


Figure 6: FT-IR Spectrum for Dye D

Acknowledgements

The authors appreciate the Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

REFERENCES

[1] Bulearca, M., Bulearca, A., & Sebe, I. (2006). Synthesis Of Reactive Dyes Based On Epychlorohydrine. *University Politehnica of Bucharest Scientific Bulletin Series B-Chemistry and Materials Science*, 68(3), 21-32.

[2] Lykidou, S., Karanikas, E., Nikolaidis, N., & Tsatsaroni, E. (2016). Azo reactive dyes: ultrafiltration and application to cotton by exhaustion and digital ink-jet printing. *Textile Research Journal*, 86(8), 823-836.

[3] Ahmed A. Farag, Hassan S. Mahmouc, Ahmed M. G. Nassa and Ahmed Shawki (2008). Studies on Some New Reactive Disperse Dyes, *Journal of the Society of Dyers and Colourists*, 96, 3, (126-132).

[4] Patel D. R., Patel N. S., Patel H. S. and Patel K. C., (2001). Synthesis, characterization and application of novel bisazo reactive dyes on various fibers, *Orbital: The Electronic Journal of Chemistry* 3, 57.

[5] Chen, K. (2007). Analysis of reactive dye mixtures-characterization of products from bis-dichlorotriazine dye synthesis. A thesis submitted to North Carolina University

[6] Fergusson, S. M. (2008). The effect of laundry detergents and residual alkali on the light fastness of reactive dyes on 100% cotton. A thesis submitted to the RMIT University

[7] Batchelor, S. N. (2015). New insights into dye chemistry and physics. *Coloration Technology*, 131(2), 81–93. doi:10.1111/cote.12138

[8] Lewis, D.M. (1992). Wool Dyeing, *Society of Dyers and Colourists*, 222-256.

[9] Lee, Y. H., & Pavlostathis, S. G. (2004). Decolorization and toxicity of reactive anthraquinone textile dyes under methanogenic conditions. *Water Research*, 38(7), 1838-1852.

[10] Ojstršek, A., Doliška, A., & Fakin, D. (2008). Analysis of reactive dyestuffs and their hydrolysis by capillary electrophoresis. *Analytical sciences*, 24(12), 1581-1587.

[11] Patel, D. R., & Patel, K. C. (2010). Synthesis, characterization and application of quinazolinone based reactive dyes for various fibers. *Fibers and Polymers*, 11(4), 537-544.

[12] Gamit, E. A., Patel, S. M., & Savant, S. S. (2017). Synthesis, Characterization and Applications of Some New Reactive Dyes based on 5, 5'-methylenebis (2-aminobenzenesulfonic acid). *International Journal of Chemical Sciences*, 15(2), 142.

[13] Antonio, E.H.M., Neuton, M.B., Ligia, M.R., Nkeonye, P.O. & Radim, H. (2008). Study of the spectroscopic properties and first hyperpolarizabilities of disperse Azo dyes derived from 2-amino-5-nitrothiazole. *Journal of Photochemistry and Photobiology A: Chemistry* 199 (1), 23–33.

[14] Shenai V. A. Chemistry of Dyes and Principle of Dyeing, Sevak Publication, Mumbai. 1973.

[15] Cox, D. M. (1999). High surface area materials. In Nanostructure Science and Technology (pp. 49-66). Springer, Dordrecht.

[16] Akaranta, O. & Agiri, G. O., (2010) Synthesis and characterisation of reactive dye-cassava mesocarp cation exchange resins. *African Journal of Biotechnology*, 9 (20), 2977-2984