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SYNTHESIS, CHARACTERIZATION AND DYEING PROPERTIES OF NYLON 6.6 AND WOOL WITH A DISPERSANT-FREE AZO REACTIVE DISPERSE DYE

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ABSTRACT

This paper examines the synthesis of a novel dispersant-free azo reactive disperse dyes obtained by using para derivatives (2,4-dibromo) as the substituents in the coupling components 2-amino-4- (2,4-dibromo phenyl) thiophene-3- carbonitrile with monochlorotriazine (MCT)/sulphatoethylsulphone (SES) diazo component. The study aims at eliminating the major problem of reactive dyes which is incomplete fixation and hydrolysis. The coupling component and synthesized dyes were purified by recrystallization and the purity was tested by thin-layer chromatography using pre-coated silica gel G plates. Dyes were characterized by Proton and Carbon NMR, GC/MS and Infra-red analysis. The spectroscopic properties of the dye in various solvents were also examined and the dye showed a bathochromic shift when the solvent was changed to more polar solvents. The dye also showed positive and negative halochromism with the addition of a few drops of hydrochloric acid (HCl) at a concentration of 2 X 10^{-5}mol/dm^3. The dyeing performance of the dye was evaluated on wool and nylon 6.6 fabrics. The introduction of two temporarily anionic sulphatoethylsulphone (SES) and monochlorotriazine (MCT) reactive groups into the reactive disperse dye molecule was found to promote the fixation and the buildup. The dyed fabrics showed good to moderate light fastness rating of 4 for wool and 5 for nylon 6.6 as well as very good to excellent wash fastness ratings of 3-4 for wool and 4-5 for nylon and perspiration rating of 4-5 for both wool and nylon 6.6 respectively. The dye bath exhaustion on wool and nylon 6.6 was found to be very good and the fixation values were 72% for wool and 61% for nylon 6. This study showed that dyes containing MCT and SES groups possess better fastness and fixation properties than convectional azo disperse or reactive dyes which can be attributed to the covalent bond formed between the dye molecules and the fibre.

KEYWORDS

Diazotization, dispersant -free, reactive-disperse, exhaustion and fixation studies

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INTRODUCTION

Several goals have also been achieved by the use of reactive disperse dyes which possessed the features needed for the affinity for any of the widely used fibre types without the need to conduct separate reactions outside the dye bath (Suwanruji et al., 2004). Azo dyes are the most used dyes and account for more than 60 % of total dyes (Gurses et al., 2016, Shah et al., 2014). Approximately 70 % of all the dyes used in industry are azo dyes (Lipskikh et al., 2018, Berradi et al., 2019), considering the biological importance of azo compounds and their vast applications in industry and pharmacy (Obu et al., 2021), plastics, hypnotic medicine, living cells cancer and pharmacological activities (Dembitsky,2017), biological, in high-tech applications such as lasers and nonlinear optical systems, thermal transfer printers and fuel cells. Also sensitized to solar cells (El Mekkawi & Mottaleb, 2005), metallochromic indicators (Etesami et al., 2019), dyeing of textiles (Lucas et al., 2007, Odey 2022), leather, paper, food (Dhungana 2019), cosmetics (Khalid et al., 2008). These compounds are characterized by the functional group (-N= N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals. Azo dyes are the most important synthetic colorants which have been widely used in textile, printing, paper manufacturing, etc. (Benkhaya & Harfi 2017).

In recent years several attempts have been made to produce different types of reactive disperse dyes for example, reactive disperse dyes carrying MCT (De Giorgi & Cerniani 1987), Vinylsulphone (Nishida & Ando 1981) MCT/SES (Ishegbe et al., 2019) and disulphide bis (ethylsulphone), reactive groups. All these exhibited dyes as monofunctional dyes. Reactive dyes react chemically with amino groups within the nylon fibre to form a covalent bond. Theoretically, by virtue of the covalent nature of the dye-fibre bond, reactive dyeing on nylon fibres can display excellent wash fastness without any recourse to an after-treatment, especially, reactive dyes containing heterobifunctional groups can provide great opportunity for efficient dye-fibre reactions due to the SES and monochlorotriazininyl reactive systems (Ishegbe et al., 2020). Reactive disperse dyes containing β-sulphatoethylsulphone (SES) group have been extensively reported. In an earlier study, Dohmyou et al 1990 applied reactive disperse dyes containing SES group to silk, polyester and nylon fabrics. These studies investigated reactive disperse dyes as monofunctional dyes with problem of incomplete fixation of dyes leading to hydrolysis and environmental pollution and degradation.

Some previous studies also reported the synthesis of homobifunctional reactive disperse dyes having bis (SES) reactive groups applied on nylon 6 and silk (Youssef, 2009) and heterobifunctional dyes on nylon 6.6 and polyester (Ishegbe et al., 2019). These studies illustrated that the bi functional dye fixed effectively to silk, nylon 6.6 and nylon 6 with improved application properties being accounted to its highly non-ionic reactive bis -vinyl sulphone system under alkaline conditions. By virtue of the characteristic dye structure reactivity, excellent levelling and fastness properties were also obtained. However, the synthesized dyes did not give complete fixation and were not applied to wool substrate.

Some other studies reported heterobifunctional reactive disperse dye having SES reactive group combined with disulphide bis (ethylsulphone) reactive group which have been applied on nylon 6 fabric (Broadbent, 2001) and nylon 6.6 (Ishegbe et al., 2020). This bifunctional reactive disperse dye exhibited high exhaustion and fixation values at pH 6 and 120 °C. The results also indicate that the combination of temporarily anionic and non-ionic reactive groups of the bifunctional dye provided great enhancement in dyeing performance compared to that of the monofunctional dye. The dyes also showed very good levelling and fastness properties on nylon 6 fabric.

Considering the numerous applications of nylon, the textile industry has been under pressure to produce high quality dyed nylon or polyamide with excellent coverage of substrate variations and high wet fastness (Petrova, 2005). According to Soleimani and Taylor 2006, both fastness and levelness properties are of great importance in nylon dyeing, choosing dyes that overcome both concerns is challenging. This can be overcome by the emergence of reactive disperse dyes which are disperse dyes bearing reactive groups in their structure, integrating the desirable characteristics of both disperse dyes and reactive on nylon, hence the need for this study. This paper examines the synthesis and evaluation of a monoazo bifunctional reactive disperse dye obtained by coupling 2-amino-4- (2,4-dibromophenyl) thiophene-3- carbonitrile with MCT /SES diazo component, whereby a simple mono azo SES dye was condensed with cyanuric chloride forming the target mono azo bifunctional reactive disperse dye containing the thiophene moiety (Scheme 1).

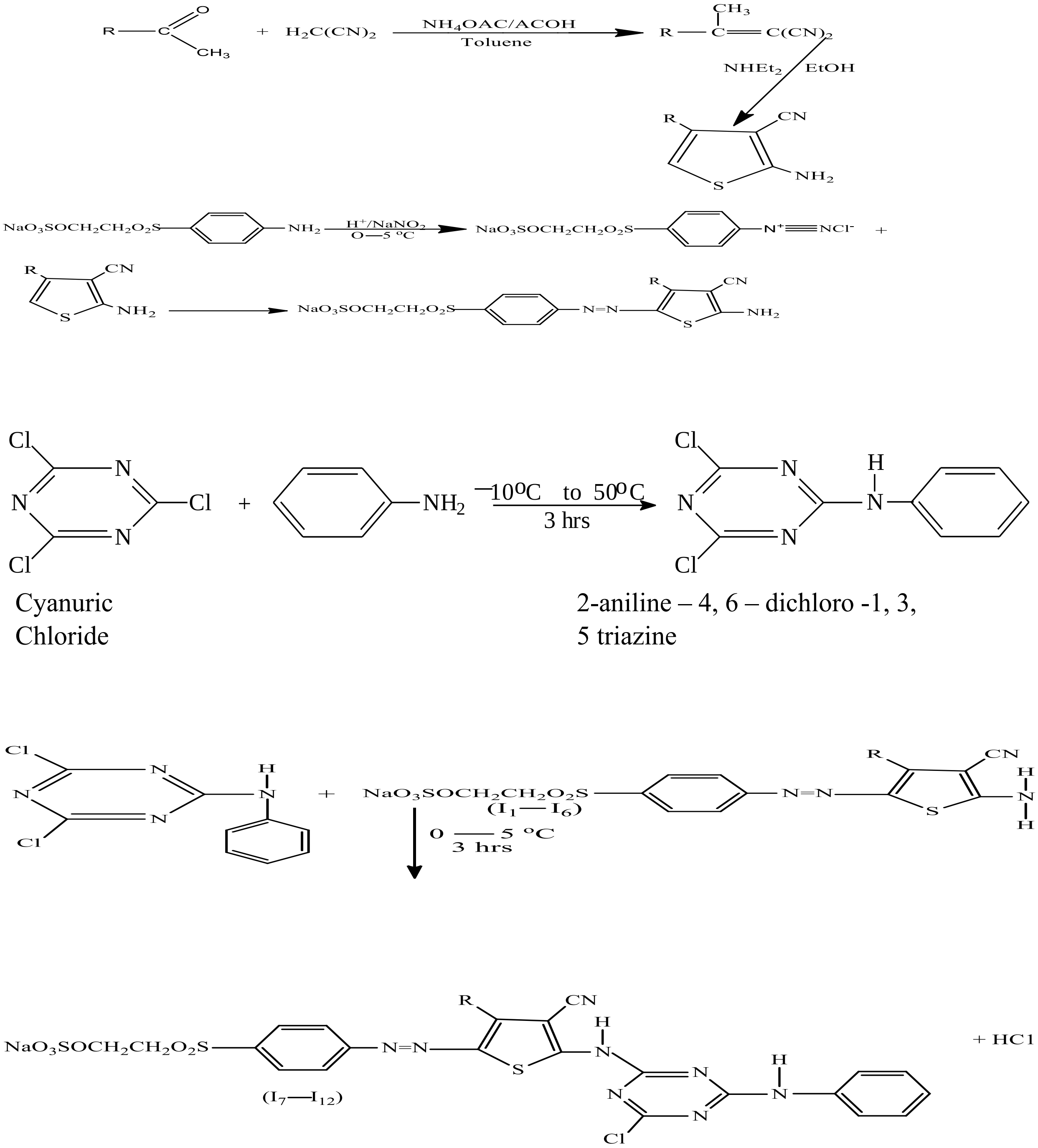
MATERIALS AND METHOD

All the chemicals used were purchased from different vendors like Sigma Aldrich, Dayang chemicals, Ievakluga, Synquest laboratory and King scientific and were used without further purification. The major chemicals include malononitrile, para substituents of acetophenone (bromoacetophenone, and 2,3-dibromoacetophenone), ammonium acetate, sulphur, acetone, diethyl ether, toluene, hydrochloric acid, sodium nitrite, ethanol.

Synthesis of dyes I6 and I12.

A well stirred solution of 1-aminobenzene-4-β-sulphatoethylsulphone (10.2 g, 0.05 mol) in 2 N HCl (15 ml) was cooled at 0^{o}C - 5^{o}C in an ice bath and diazotized with 1 N $NaNO_2$ solution (3.5 g, 0.05 mol; in 20 ml water). The sodium nitrite was added drop wisely over 30 minutes while stirring. The reaction mixture was stirred for another 2 hours. A small amount of urea (0.5 g) was also added to destroy excess nitrous acid. (Ishegbe & Bello 2014). The above cold solution of the diazotized 1-aminobenzene-4-β-sulphatoethylsulphone (14.8 g, 0.05 mol at 95% purity) was reacted with 2-amino-4-p (2,4-dibromophenyl) thiophene (4.9 g, 0.05 mol) in distilled water (25 ml) and hydrochloric acid (6 ml, 36%) over 30 min at 0-5°C. The mixture was stirred for 3 hours, maintaining the temperature below 5°C and the pH at 3.5 - 4. (Ishegbe et al., 2022). The mono azo reactive disperse dye obtained (I6) was filtered off and dried at room temperature and weighed.

The dispersant free bifunctional azo reactive dye was obtained by condensation of cyanuric chloride with aniline. The product was prepared from equimolar amounts of analogous starting materials in toluene solution at a temperature of -10^{o}C to 50^{o}C. Cyanuric chloride (9.22 g, 0.05 moles) was reacted with aniline (27 g, 0.3 moles) at a molar ratio of 1: 6. The compound (2-aniline-4, 6-dichloro-1, 3, 5-triazine (0.05 moles) was further reacted in ratio of 1:1 with the mono azo reactive disperse dyes (I6) earlier obtained, at a temperature of 0-5^{o}C for 3 hours to get the hetero bifunctional azo reactive disperse dyes (I12).



R = ($C_6H_3Br_2$)

Scheme 2: Synthesis of bifunctional azo reactive disperse dye

Melting point determination and characterization of synthesized dyes

Melting points were determined using melting point apparatus in open capillaries and are uncorrected. After work-up was completed, (unreacted starting materials were removed by washing with ether), the products were subjected to purification by recrystallization process. Again, TLC was run to find out exact Rf value. TLC plates used for final recrystallized product were pre-coated silica gel G plates. The infra-red spectra were carried out on FTIR Nexus 670 spectrophotometer in KBr disc (Thermo Nicolet) and absorption bands are expressed in cm-1. Mass spectra were recorded on an Agilent Technologies 6460 Mass Spectrometer using the electron spray ionization (ESI) technique. The data shows peaks at $[M+H]^+$ and $M+Na]^+$. H^+NMR and CNMR were recorded using TMS-tetramethylsilane as internal standard and chemical shifts are given in δ (ppm), while coupling constants values were in HZ. The chemical shifts are positioned in relation to a reference proton set at 0.00 ppm. Tetramethylsilane $(CH_3)_4Si$), is the standard for H^+NMR.

Dyeing of nylon 6.6 and wool with i6 and I12

The stock solution of each dye was prepared by weighing 0.3g dye powder and adding it to a beaker containing 20ml aqueous dimethylformamide (DMF). Nylon 6.6 and wool fabrics were dyed using the synthesized azo reactive disperse dye in a dyeing machine with 1g sample at a Liquor ratio 50:1. The dye bath was prepared at room temperature in the presence of dye concentrations (1-5 % owf). The dye bath was prepared at pH 2, 4, 6, 8, 10 and 12 using sodium carbonate and acetic acid solutions. Dyeing started at 40°C and then the temperature was raised to 100°C over 60 min. Dyeing was continued at the desired temperature for a further 45 min (105 min total dyeing) (Ishegbe et al., 2019) the percentage yield of dyes was determined.

Determination of percentage exhaustion of dyes

The uptake of the polyfunctional reactive disperse dyes by nylon 6.6 and wool fabrics was measured by sampling the dye bath before and after dyeing (Ishegbe et al., 2014). The dye concentration (g/L) of the dye bath, diluted with 25ml acetone, was measured spectrophotometrically at the λmax value. The percentage of dye bath exhaustion (%E) was calculated using Equation 1

$$\%E = \left[\left(\frac{A_1 - A_2}{A_1} \right) \right] x100 \quad ....(1)$$

A_1 and A_2 are the dye absorbance in the dye bath before and after dyeing respectively.

Determination of dye fixation

The dye fixation (%F) i.e the percentage of the exhausted dye chemically bound on the fibre, was measured by stripping and refluxing the dyed samples in 50% aqueous DMF (20:1) for 30 min at 100°C to extract the unfixed dye.

$$\%F = \frac{(C_1 - C_2 - C_3)}{C_1 - C_2} x100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Where C_1, C_2 and C_3 is the concentration of the dyebath before dyeing, after dyeing and the concentration of extracted dye respectively. From the dyebath exhaustion (E) and dye fixation (F), the total dye fixation (T), which is the percentage of dye chemically bound relative to the total amount of dye used, was calculated for all dyeing using Equation 3 (Burkinshaw *et al.*, 2001).

$$\%T = \frac{(\%E \; x \; \%F)}{100} \quad \text{...(3)}$$

Determination of fastness test

The dyed samples will be tested by the standard ISO methods (Methods of test, 1990). The tests are as follows: Colour fastness to washing, ISO 105-C02 (1989); ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); and fastness to light using microsal tester xenon lamp.

Fastness to washing:

The I.S.O 105-C02 standard procedure for washing was used to determine the wash fastness test. The washing conditions are as follows. Soda ash 2g/l, Soap 5g/l, Liquor ratio 50:1, Temperature 60 ± 2 ^oC, Time 30 minutes. The test was carried out for wool and nylon 6.6 fabrics respectively. A composite specimen was prepared by stitching the dyed samples of size 10 cm x 4 cm between an undyed wool and undyed cotton and size 10 cm x 4 cm between an undyed cotton and undyed nylon respectively. The composite specimen was agitated in 100 ml beaker containing the soap solution, plus other additives as mentioned above in the specified conditions of liquor ratio, temperature and time. The composite specimen was then removed, rinsed and the components separated and dried. The change in colour of the dyed samples and the staining of the adjacent undyed cloths were assessed using the appropriate grey scales.

Fastness to light:

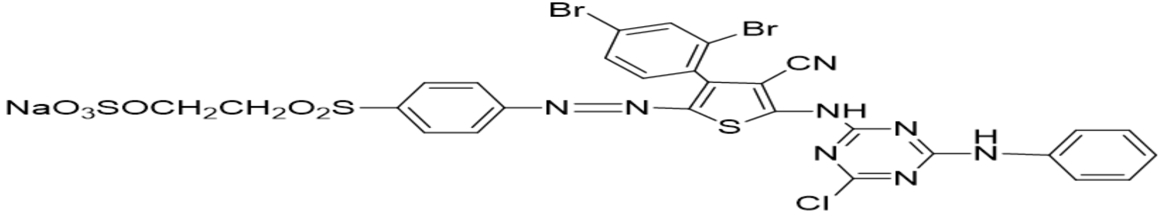
The colour fastness to light was carried out according to standard (ISO 105-B02) using the Microsal light fastness tester model no 225" James Heal & co ltd. The samples of the test specimens (nylon 6.6 and wool respectively) were cut into 5 cm X 2 cm according to the length and width wise respectively and attached with the sample specimen holder. The holder was set into the Microsal light fastness tester and exposed under intense artificial illumination. Another holder carrying the eight blue wool standards was placed into the tester. Then the samples were exposed to the UV radiations for 72 hours after which the specimen were taken from the light fastness tester and were compared with the blue wool scale for light fastness rating.

Fastness to perspiration:

This was done using an acid solution and alkaline solution containing the following respectively: 10g/l sodium chloride (NaCl),1g/l sodium dihydrogen orthophosphate, 0.25g/l 1-histidine monohydrochloride ($C_6H_9O_2N_3HCl$), pH 5.5(acetic acid solution) for acidic solution and 10g/l sodium chloride (NaCl), 1g/l sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$), 0.25g/l histidine monohydrochloride ($NaH_2PO_4.2H_2O$) ($C_6H_9O_2N_3HCl.H_2O$), pH 8 (0.1 sodium hydroxide solution for alkaline condition respectively.

RESULT AND DISCUSSION

This was achieved by condensing acetophenone with malononitrile in toluene using a heterocatalytic system. The reaction mixture was refluxed in the presence of catalytic amount of acetic acid and ammonium acetate to produce arylidenemalononitrile as an intermediate, followed by the cyclisation with Sulphur to give the desired products.



sodium 2-((4-((5-((4-chloro-6-(phenylamino)-1,3,5-triazin-2-yl)amino)-4-cyano-3-(2,4-dibromophenyl)thiophen-2-yl)diazenyl)phenyl)sulfonyl)ethyl sulfate

Figure 1: Structure of the synthesized dye

The dyes had good percentage yield of between 50% to 58% with bright colours of yellow and grey. The colour of the azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. The azo dyes are generally characterized by a chemical group capable of forming covalent bonds with the nylon 6.6 and wool substrates. The energy required for the rupture of these bonds is similar to that used to degrade the support itself (Said et al., 2022). The physical properties of the dyes are shown in Table 1 below.

Table 1: Physical properties of the synthesized dyes

Dye code	Empirical formula	Molecular mass ($gmol^{-1}$)	Melting point (°C)	Yield (%)	Colour of crystal
I_6	$C_{18}H_{16}O_6N_3S_3Br_2$	625.8	168-170	50	Grey
I_{12}	$C_{27}H_{21}O_6N_7S_3Br_2Cl$	794.8.	160-162	58	yellow

The molar extinction coefficient (ε), which is a constant for each molecule at any given wavelength, representing the absorbance of a 1cm thickness of a medium containing 1 mole of the absorbing substance per litre (ε) was calculated using the relationship:

Log 10(Io/I) absorbance A or optical density:

$$\varepsilon = A/Cl$$

where ε = extinction coefficient, A= Absorbance, C = concentration of the dye in mol/dm^3 and L = path length in cm

Visible absorption spectra:

The Visible absorption spectra were measured using CARY 630 UV-visible spectrophotometer Model Agilent technology and they were measured from dye solutions in acetone, ethanol, ethanol plus few drops of hydrochloric acid at a concentration of $2 \times 10^{-5} mol/dm^3$. The results are shown in table 2 below.

Table 2: Visible absorption data of dyes

Dyes	**εmax 10^5 Lmol $^{-1}$cm^{-1} in EtOH**	**Ethanol λ max (nm)**	**Acetone λ max (nm)**	**Ethanol + HCl λmax(nm)**	**Chloroform λ max(nm)**	**Change in λmax (nm)**
I6	5.0	410	408	437	401	-27
I12	2.23	400	400	402	400	-2

The maximum absorption wavelength increased with increase in solvent polarity. Bathochromic shifts of the visible absorption band were also observed on increasing the solvent polarity where the difference in λmax was noticed upon measuring the dyes in Ethanol and acetone.

Infra-red data:

The functional groups that made up the structure of the intermediates were confirmed by infra-red spectrum on FTIR Nexus 670 spectrometer in KBr disc (172hermos nicolet) while the infra-red spectra of the dyes were carried out on CARY 630 FTIR–Agilent technologies. All absorption bands are expressed in cm^{-1} and are shown in Table 3 below.

Table 3: Infra-red data of the synthesized dyes

Functional group	**C=C**	**C-H**	**C=C**	**N-H**	**Ar-H**	**C-S**	**C-N**	**C-C**	**N=N**	**C-H**	**C-Br**	**C-H**
Type of vibration	Bending Ali	Bending aro	Str	Str	Str Ar	In-plane bend	Str	Str ali	Str ali	In-plane of Ar-H		Str ali
I$_6$	1640		1580		3086	719	1062	1244	1484	1140		2307
I$_{12}$	1625	827	1584	3652	3049	685	1039	1293	1494		723	2232

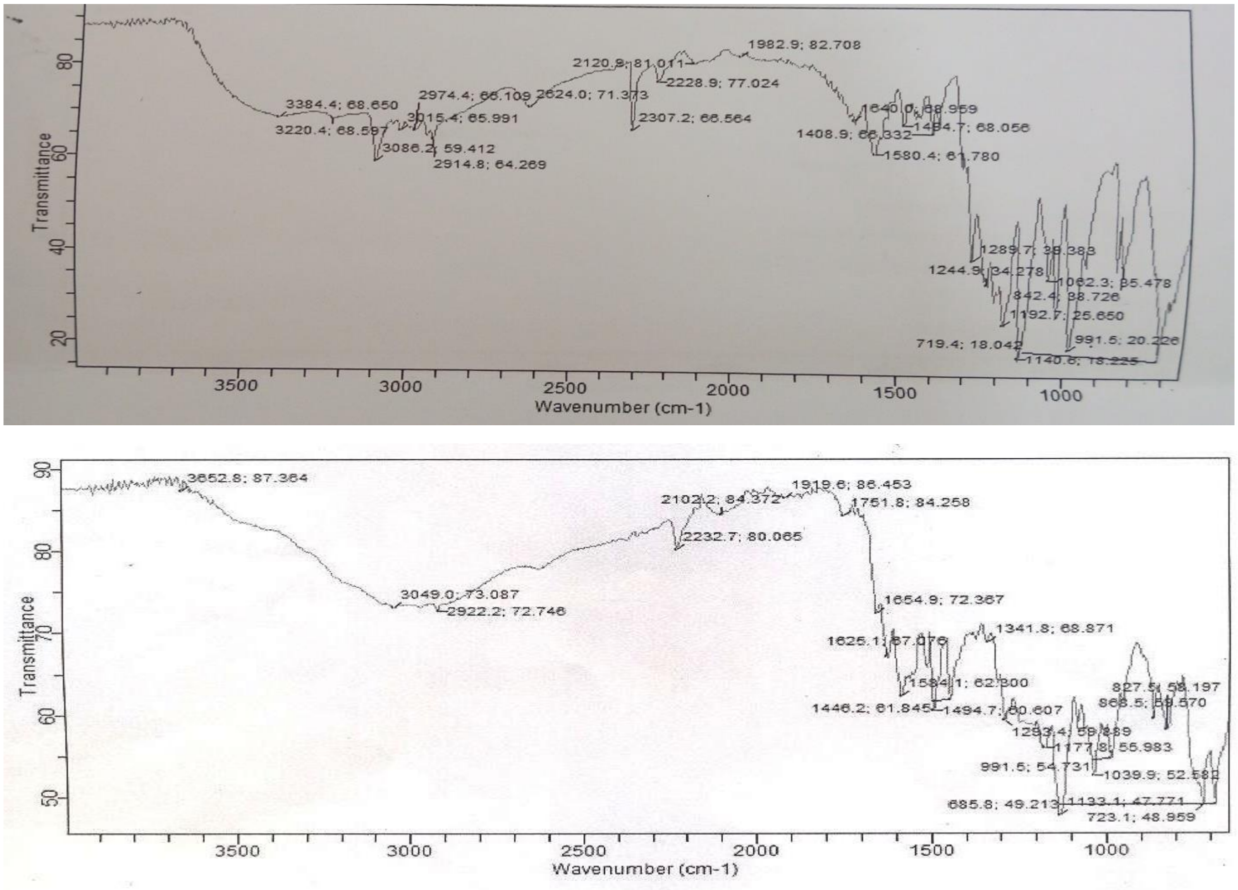


Figure 2: Infra-red spectra of the synthesized dye I6 and I12 respectively.

Mass spectrometry:
Mass spectra were recorded on an Agilent technologies 6460 mass spectrometer using the electron spray ionization (ESI) technique. The data shows peaks at [M+H] $^+$ and [M+Na] $^+$

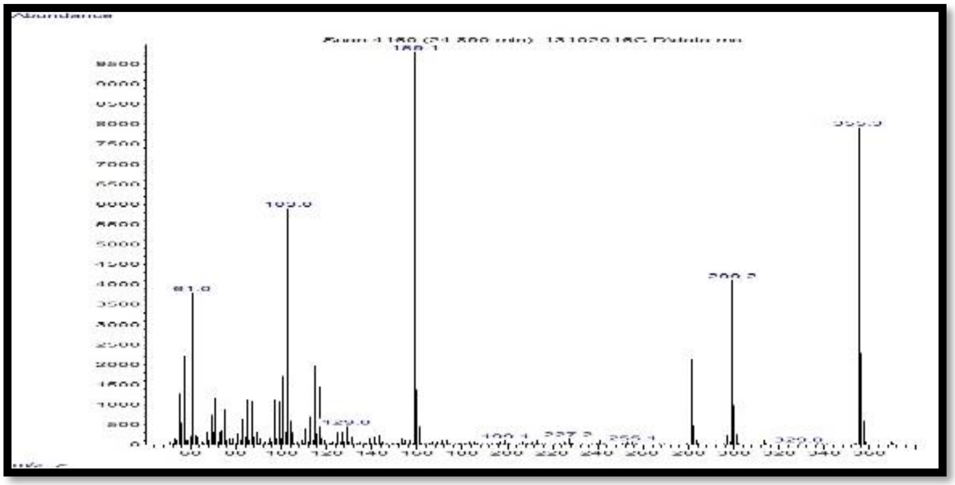


Figure 3: Mass spectra for AI6

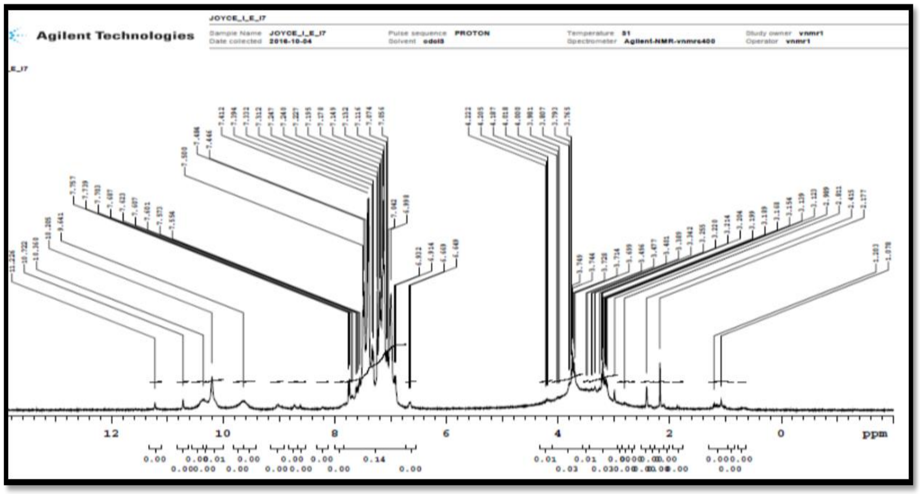


Figure 4: HNMR OF I6

Dyeing procedure

Wool, and Nylon 6.6 fabrics were dyed using the synthesized azo reactive disperse dye in a dyeing machine with 1 g sample at a liquor ratio 50:1. The dye bath was prepared at room temperature in the presence of dye concentrations (1-5 % owf). The dye bath was prepared at pH 4, 5, 6, 7 and 8. Dyeing started at 40 °C and then the temperature was raised to 100 °C over 60 min. Dyeing was continued at the desired temperature for a further 45 min (105 min total dyeing time). After dyeing, all dyed samples were rinsed with running water and air dried. Dye exhaustion and total dye fixation on wool and nylon 6.6 fabrics were evaluated spectrophotometrically (Mohammed et al., 2013). The results shows that they had good exhaustion values on both wool and nylon.

Effect of pH on dye exhaustion

With other conditions constant, the effect of pH on dye exhaustion was determined by varying the pH from 2, 4, 6, 8, 10 and 12 at an interval of 2. A pH of 6 and 8 was found to give optimum results and high exhaustion values of 60 and 68 for monofunctional and bifunctional dyes respectively. This is in conformity with a work carried out by Petrova 2005, who synthesized novel azo reactive disperse dyes and obtained good exhaustion under alkaline condition.

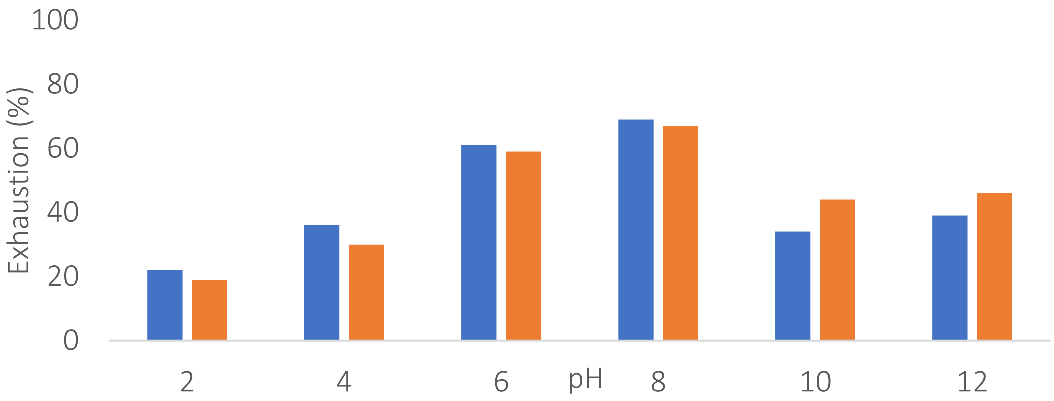


Figure 5: Effect of pH on dye exhaustion on nylon 6.6 using dyes I6 and I12

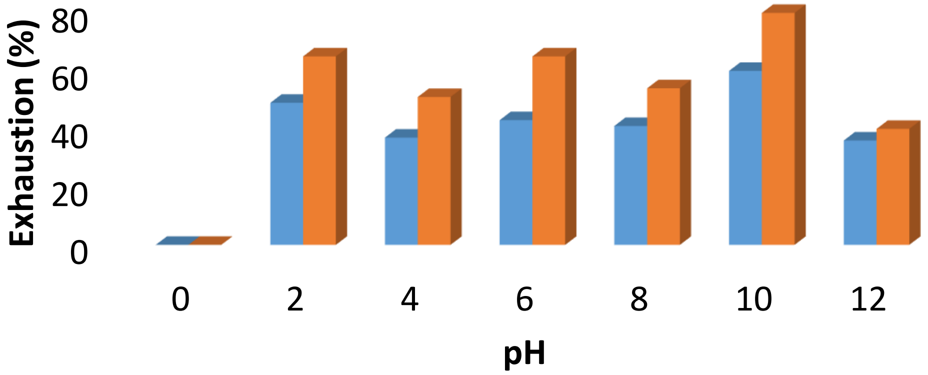


Figure 6: Effect of pH on dye exhaustion on wool using dyes I6 and I12

Effect of time on dyeing: The effect of dyeing time on dye exhaustion was carried out by varying the time from 15 minutes to 60 minutes at an interval of 15 minutes each. Results shows that optimum dyeing time was at 60 mins. Extension of dyeing time to 105 minutes showed no significant increase in exhaustion.

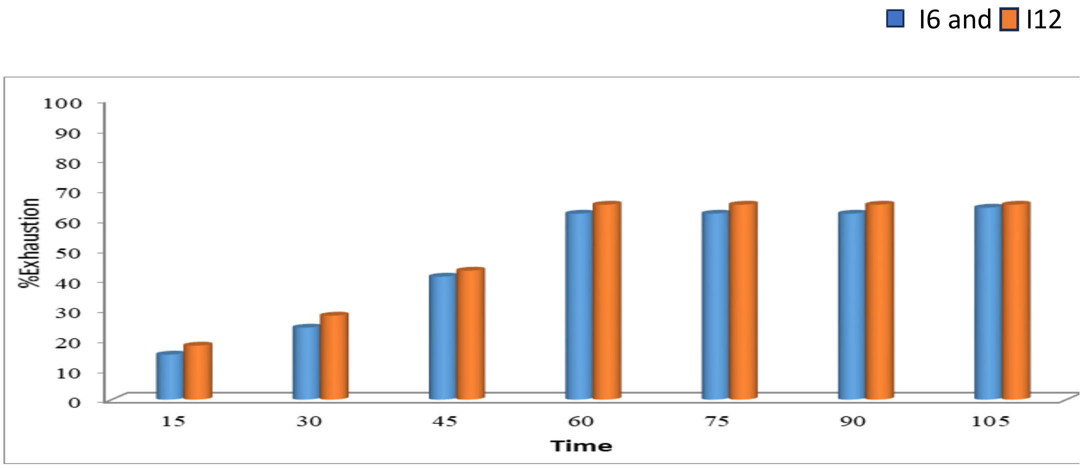


Figure 7: Effect of dyeing time on exhaustion on wool using dyes I12 and I6

Effect of temperature on dyeing: The effect of temperature on dye exhaustion was carried out by varying temperature from $40^{o}C$ to $100^{o}C$ at an interval of $10^{o}C$. results show that as the temperature increases, exhaustion also increases. This is as a result of increase in the kinetic energy of the dye molecules as well as increase in the pores of the fabric at high temperature. This aligns with the results obtained by Debrasree 2017, whereas the temperature increases from $40^{o}C$ to $80^{o}C$, the molecular structure becomes open which facilitates dye uptake for fabrics and hence the higher colour strength (K/S) of 0.04 is obtained.

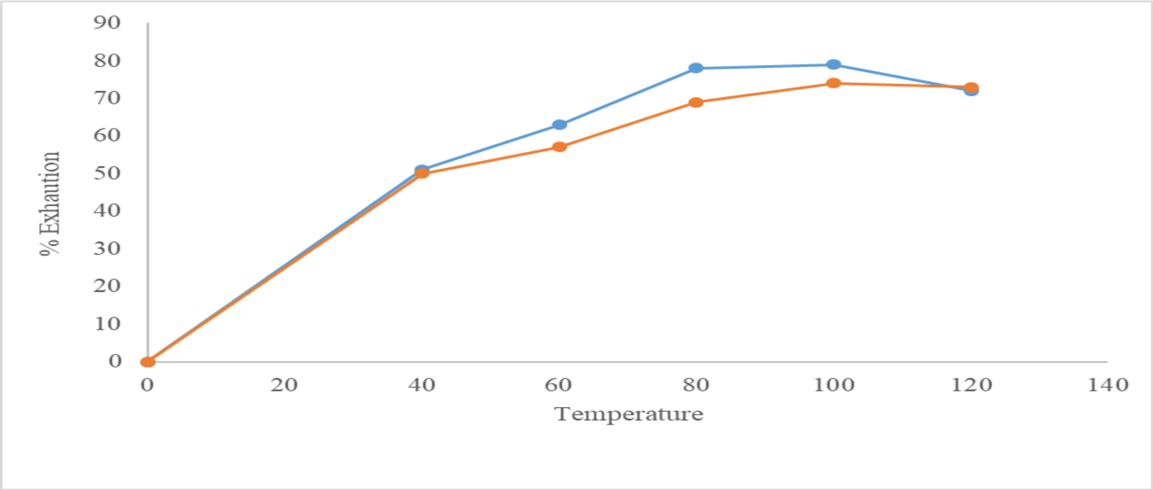


Figure 8: Effect of temperature on exhaustion on nylon 6.6 using dyes I16 AND I12

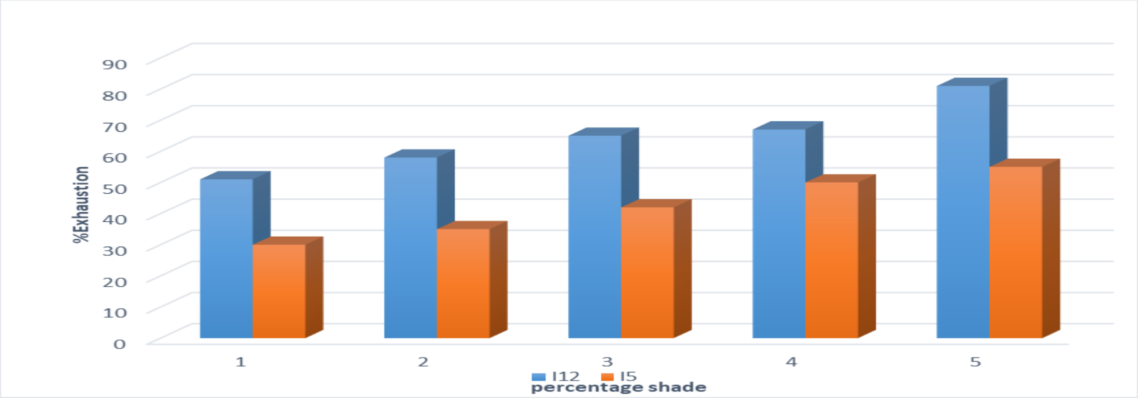


Figure 9: Effect of percentage shade on dye exhaustion on nylon 6.6 using dyes I12 and I6

Measurements and testing

Dye exhaustion: The uptake of the polyfunctional disazo reactive disperse dyes by nylon 6.6 and wool fabrics was measured by sampling the dye bath before and after dyeing. The dye concentration (g/L) of the dye bath, diluted with 25 ml acetone, was measured spectrophotometrically at the λmax value. The percentage of dyebath exhaustion (% E) was calculated using Equation 1 (Burkinshaw et al., 2001). It was found to possess good exhaustion values. The percentage fixation of dyes on wool and nylon were good from 43 to 72 for wool and 59 to 61 for nylon respectively. This agrees with a work done by Raju et al., 2022 whose synthesized dyes when applied had significant improvement in the colour strength and dye fixation efficiency. According to Raju et al., 2022, this is due to the formation of covalent bond between the amine(-NH_2) and the hydroxy (-OH) group of the fabrics.

The dye build-up in this study is also in conformity with a work done according to Kong & Burkinshaw 1996 where the dye build-up of his synthesized dye increased with increasing pH of application from 2 to 10. This dyeing method produced minimal amount of waste water as no chemical additives was added to the dyebath as dyes synthesized can be applied without the use of a dispersing agent. Hence little or minimal dye liquor is left to be released into the environment. However, the unfixed dye in the effluent or waste water was purified by sorption method to give nearly 100% pure water before disposal. Purification is always a considerable concern for green and environmental safety.

Table 4: Percentage fixation of the dyes on wool and nylon 6.6

Dye code	Wool	Nylon
I6	43	61
I12	72	59

Fastness testing:

The dyed samples were tested by the standard ISO methods. The tests are as follows: Colour fastness to washing, ISO 105-C02 (1989); fastness to rubbing, ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); and fastness to light. Table 5 shows that it had excellent fastness to washing values of 4-5 and staining of adjacent cotton of 4-4 showing that the dye is fixed unto the fabric. It also had good to moderate light fastness values as shown in table 6 and fastness to perspiration ratings of 4 and 4-5 under acidic and alkaline condition respectively as shown in table 7. This agrees with the investigation carried out by Nadia & Mohammed 2017, where the synthesized disperse and reactive disperse dyes containing dichlorotriazine group has better fastness properties of 4-5 than that of the conventional azo disperse dye.

Table 5: Wash Fastness ratings for the synthesized dyes on nylon 6.6 and wool

Wash fastness on nylon 6.6				**Wash fastness on wool**		
Code	Change in colour	Staining on cotton	Staining on nylon	Change in colour	Staining on cotton	Staining on wool
I_6	4	4-5	4	3	3-4	4
I_{12}	4	4	4	4	4	4

Table 6: Light fastness ratings on wool and nylon 6.6

Dye code	Rating on wool	Rating on nylon 6.6
I_6	4	5
I_{12}	4	3

Table 7: Fastness to Perspiration ratings under acidic and alkaline condition.

	Acidic condition			**Alkaline condition**		
Dye code	Change in colour	Staining on cotton	Staining on Nylon 6.6	Change in colour	Staining on nylon 6.6	Staining on cotton
I6	4	4	4	4	4-5	4-5
I12	4	4	5	4-5	4-5	4-5

The fixation values were good for the synthesized bifunctional dyes due to moderate hydrolysis. The dyeability of wool was better than on nylon and the fixation values were slightly higher on wool than on nylon fabrics. This is probably because wool has ten times more dyeing sites than nylon 6.6 The fastness properties were better on nylon than on wool for wash and light fastness properties.

CONCLUSION

Synthesis of azo disperse reactive dyes containing MCT/SES with thiophene moiety has attracted the attention of many researchers because of their unique properties and substantial advantages of high fixation, level dyeing, colour uniformity and good build up. This study is helpful for industrial and sustainable dyeing process as it can find applications on both natural and synthetic fabrics, as these dyes possess excellent coverage of substrate variations and high wet fastness. This work has provided useful synthesis pathway to obtain novel bifunctional azo reactive disperse dyes with MCT/SES reactive groups containing aminothiophene moiety. The synthesized dyes have attempted to eliminated the major problem of reactive dyes which is incomplete fixation leading to hydrolysis and colour effluent and this has served as a contributor to green chemistry. The synthesized dyes can be applied on substrate without the use of dispersing agents. The synthesized dyes showed good build-up and fastness properties when applied to wool and nylon 6.6 fabrics and they can be applied on any fabric as well.

REFERENCES

Benkhaya, S., & El Harfi, A. (2017). Classifications, properties, and applications of textile dyes: A review. *Applied Journal of Environmental Engineering Science, 3*, 00000-3.

Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon, 5*(e02711). https://doi.org/10.1016/j.heliyon.2019.e02711

Broadbent, A. D. (2001). *Basic principles of textile coloration*. Bradford: Society of Dyers and Colourists.

De Giorgi, M. R., & Cerniani, A. (1987). Dyeing kinetics of monofunctional dyes for nylon. *Textile Research Journal, 57*, 563. https://doi.org/10.1177/004051758705701002

Debasree, P., Subrata, C., Tarikul, I., Abubakar, S. M., & Abdullahi, A. M. (2017). Effect of temperature on dyeing cotton knitted fabrics with reactive dyes. *Journal of Scientific & Engineering Research, 4*(12), 388-393. https://doi.org/10.17265/1934-7375/2017.04.004

Dembitsky, V. M., Gloriozova, T. A., & Poroikov, V. V. (2017). Pharmacological and predicted activities of natural azo compounds. *Natural Products and Bioprospecting, 7*, 151-169. https://doi.org/10.1007/s13659-016-0117-3

Dhungana, B., Peng, H., Kutarna, S., Umbuzeiro, G., Shrestha, S., Liu, J., ... Cobb, G. P. (2019). Abundances and concentrations of brominated azo dyes detected in indoor dust. *Environmental Pollution, 252*, 784-793. https://doi.org/10.1016/j.envpol.2019.05.153

Dohmyou, M., Shimizu, Y., & Kimura, M. (1990). Simultaneous dyeing of silk and synthetic fibres with sulphatoethylsulphonyl reactive disperse dyes. *Journal of the Society of Dyers and Colourists, 106*, 395. https://doi.org/10.1111/j.1478-4408.1990.tb01236.x

El Mekkawi, D., & Abdel-Mottaleb, M. (2005). The interaction and photostability of some xanthenes and selected azo sensitizing dyes with TiO2 nanoparticles. *International Journal of Photoenergy, 7*, 95-101. https://doi.org/10.1155/S1110662X05000140

Emmanuel, U., Ishegbe, J. E., Odey, J. O., Hitler, L., Victoria, M. B., & Fred, S. W. (2021). Synthesis, spectroscopic (FT-IR, excitation analysis, GC-MS), reactivity, NBO analysis, ADMET analysis, and molecular docking studies of azo dye derived from the reaction of 4-aminobenzene-4-β-sulphatoethylsulphone and 2-amino-4-(4-aminophenyl)thiophene-3-carbonitrile. *Journal of Molecular Structure*.

Etesami, H., Mansouri, M., Habibi, A., & Jahantigh, F. (2019). Synthesis and investigation of group for solar cell application. *Journal of Molecular Structure*. https://doi.org/10.1016/j.molstruc.2019.127432

Gürses, A., Açıkyıldız, M., Günes, K., & Gürses, M. S. (2016). Classification of dye and pigments. In *Dyes and Pigments* (pp. 31-45). Springer. https://doi.org/10.1007/978-3-319-33892-7_3

Ishegbe, J. E., & Bello, K. A. (2020). Dyeing of nylon 6.6 with polyfunctional disazo MCT/SES reactive disperse dyes derived from aminothiophene moiety/1-aminobenzene-4-β-sulphatoethylsulphone. *Chemical Science and Engineering Research*. https://doi.org/10.36686/Ariviyal.CSER.2020.02.04.016

Ishegbe, J. E., Bello, K. A., & Kogo, A. A. (2022). Synthesis and evaluation of coupler 4-aryl-2-aminothiophene-3-carbonitrile and its derivatives as potential coupling components in dye synthesis. *Applied Research Frontiers*. https://doi.org/10.36686/Ariviyal.ARF.2022.01.01.001

Ishegbe, J. E., Bello, K. A., & Nkeonye, P. O. (2019). Synthesis and structural-reactivity studies of bifunctional MCT/SES (monochlorotriazine/sulphatoethylsulphone) azo reactive disperse dyes applied to wool and polyester fabric. *Chemical Science International Journal, 26*(3), 1-10. https://doi.org/10.9734/CSJI/2019/v26i330094

Khalid, A., Arshad, M., & Crowley, D. E. (2008). Accelerated decolorization of structurally different azo dyes by newly isolated bacterial strains. *Applied Microbiology and Biotechnology*, *78*(3), 361–369. https://doi.org/10.1007/s00253-007-1302-4

Kong, H. S., & Burkinshaw, S. M. (1996). A study on the properties of azo disperse dyes containing ethylene derivatives (III): Application to microfibre polyester and nylon 6.6 fabrics. *Journal of the Korea Society of Dyers & Finishers, 8*(6), 445.

Lipskikh, O. I., Korotkova, E. I., Khristunova, Y. P., Barek, B., & Kratochvil, J. (2018). Sensors for voltammetric determination of food azo dyes: A critical review. *Electrochimica Acta, 260*, 974–985. https://doi.org/10.1016/j.electacta.2017.12.027

Lucas, M. S., Dias, A. A., Sampaio, A., Amaral, C., & Peres, J. A. (2007). Degradation of a textile reactive azo dye by a combined chemical-biological process: Fenton's reagent and yeast. *Water Research, 41*(5), 1103–1109. https://doi.org/10.1016/j.watres.2006.12.013

McLaren, K. (2003). *The colour science of dyes and pigments.* Adam Hilger Ltd.

Mousa, A. A., & Youssef, Y. A. (2003). Dyeing of nylon 6 and silk fabrics with a model disulphide bis(ethylsulphone) reactive disperse dye. *Coloration Technology, 119*(4), 225. https://doi.org/10.1111/j.1478-4408.2003.tb00176.x

Nadia, B. H., & Mahmoud, F. (2017). Synthesis of disperse and reactive dyes from intermediate materials and application on nylon 6. *Dyes and Pigments, 212.*

Nishida, K., & Ando, Y. (1981). Dyeing properties of reactive azo disperse dyes from *N*-ethyl-*N*-β-vinylsulphonylethyl-*m*-toluidine as coupling component and substituted 3-aminobenzothiophenes as diazo components. *Journal of the Society of Dyers and Colourists, 97,* 469.

Obu, Q. S., Louis, H., Odey, J. O., Ishegbe, J. E., Abdullahi, S., Ntui, T. N., & Oko, O. E. (2021). Synthesis, spectra (FT-IR, NMR) investigations, DFT study, in silico ADMET, and molecular docking analysis of 2-amino-4-(4-aminophenyl)thiophene-3-carbonitrile as a potential. *Journal of Molecular Structure, 1244,* 130880. https://doi.org/10.1016/j.molstruc.2021.130880

Odey, J. O., Ubana, E. I., Ishegbe, J. E., & Jones, O. O. (2022). Synthesis, characterization, and theoretical studies of the photovoltaic properties of novel bifunctional reactive disperse dyes based on aminothiazole derivatives. *Journal of Molecular Structure, 1269,* 133749. https://doi.org/10.1016/j.molstruc.2022.133749

Petrova, M., & Konstantinova, T. N. (2005). Synthesis of some reactive triazine azo dyes containing tetramethyl piperidine fragment. *Dyes and Pigments, 67,* 63–69. https://doi.org/10.1016/j.dyepig.2004.10.011

Said, B., Souad, M., & Ahmed, E. H. (2022). Classifications, properties, recent synthesis, and applications of azo dyes. *Heliyon.*

Shah, M. (2014). Effective treatment systems for azo dye degradation: A joint venture between physico-chemical and microbiological processes. *Journal of Environmental Bioremediation & Biodegradation, 2,* 231–242.

Soleimani-G., & Taylor, J. A. (2006). Dyeing of nylon with reactive dyes: Part 2. The effect of changes in the level of dye sulphonation on the dyeing of nylon with reactive dyes. *Dyes and Pigments, 68,* 119–124. https://doi.org/10.1016/j.dyepig.2005.01.012

Suwanruji, P., Freeman, H. S., & Zhao, D. (2004). Studies toward a universal dye for textile fibres. *Coloration Technology*, *120*(4), 220. https://doi.org/10.1111/j.1478-4408.2004.tb00121.x

Youssef, Y. A., Mousa, A. A., & Farouk, R. (2009). High-performance reactive disperse dye-fixation on silk fabric. *AATCC Review*, December, 33–39.