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Synthesis, Characterisation and Dyeing Properties of New Bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes based on 1,4-benzenediamine on Silk Fabric

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ABSTRACT

Series of novel bifunctional sulphatoethylsulphone (SES) azo reactive dyes were synthesized by tetrazotizing 1, 4-benzenediamine and coupling to various coupling components such as 4-nitroanilino cyanurated H-acids, 4-nitroanilino cyanurated J-acid, 4-nitroanilino cyanurated Laurent acid, 4-nitroanilino cyanurated Tobias acid and 4-nitroanilino cyanurated Gamma acid) respectively. The structures of the synthesized novel bifunctional sulphatoethylsulphone (SES) azo reactive dyes were characterized and confirmed by melting point, UV-visible spectroscopy, FT-IR spectroscopy, ^{1}H-NMR, Mass spectroscopy. The synthesised novel bifunctional sulphatoethylsulphone (SES) azo reactive dyes were applied on silk fabrics under typical exhaustion process and their dyeing properties were evaluated. The percentage exhaustion and percentage fixation of the synthesised dyes on silk fabrics were very good. All the synthesised dyes gave well to excellent properties to washing, light and perspiration respectively.

Keywords: Azo dyes; Bifunctional dyes; Exhaustion; Reactive dyes; Silk fabric.

1.0. Introduction

Oforghor *et al.*, (2020) and Ahmad *et al.*, (2012) reported that heterocyclic dyes of technical significant for application to silk fabrics are derived from tetraazo components consisting aromatic bridged diamines. The colours of tetraazo dyes containing heterocyclic rings were investigated and aromatic bridged diamines containing azo dyes have many advantages including a colour deepening effect as an intrinsic property of the heterocyclic ring (Hari and Vithal, 2002 and Alaa and Tarek, 2006).

Moreover, Ahmad *et al.*, (2012) and Akaranta *et al.*, (2012) opined that 1, 4'-benzenediamine have electron withdrawing substituent's in the three and five position hence exhibit deep colours with outstanding light fastness.. According to Patel *et al.*, (2011) and Banu *et al.*, (2013) several aromatic bridged diamines based azo dyes have been investigated, for example diazo reactive azo dyes containing substituted 3- 1,4'-benzenediamine as diazo component and vinylsulphonylethylsulphone as coupling component have been reported.

Also, disazo reactive azo dye containing disulphatoethylsulphone reactive group, was applied to silk fabric (Patel *et al.*, (2001) and Bradbury *et al.*, (2007) and as having potentially high fixation and fastness properties (Dixit *et al.*, 2010), Patel and Patel *et al.*, 2010) and Divyesh *et al.*, 2009). The affinity of these dyes was greatly enhanced by introducing a bis-sulphatoethylsulphone system into the azo dye molecule. The colour of these dyes ranges from yellow to red.

However, according to Chinta and Vijaykumar, (2013) and Castaldo *et al.*, (2017) in order to have a deep interest in understanding the role of temporarily sulphatoethylsulphone (SES) reactive group in the azo dye molecule having bathochromic shift for achieving deep colour shades, we now report the synthesis and evaluation of bifunctional sulphatoethylsulphone azo reactive dye based on 1,4'-benzenediamine as a tetrazonium component and cyanurated 4-nitroanilino acids as a coupling component.

2.0. Experimental

2.1. Materials and Methods

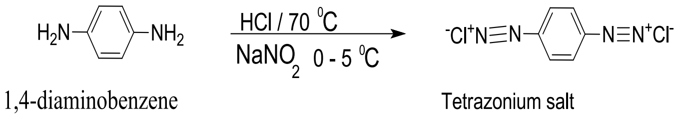
All other chemicals and solvent used in this study were of laboratory reagent grade and applied without further purification. 1,4- benzenediamine, Cyanuric chloride, H-acid, J-acid, Laurent acids, Tobias acid, Gamma acid were purchased from Weifang Senya Chemical Company Limited, China and sulphatoethylsulphone was obtained from BASF Germany. The melting points were determined by open capillary method. The UV-visible absorption spectra were recorded using Perkin-Elmer Lambda 25 UV-visible spectrophotometer (at the wavelength of maximum absorption (λmax). The FT-IR were recorded using (Perkin-Elmer Spectrum RXIFT-IR Spectrometer, ^{1}HNMR spectra were recorded using (varian 300 MHz Bruker Instrument) and Mass Spectrometer were recorded using Agilent Technologies 5975C VL MSD Mass Spectrometer at the Kharazmi University, Bureau of International Scientific Cooperation, Department of Organic Chemistry, Tehran, Iran. The silk fabric was obtained from Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria. Before application, the fabric was treated in an aqueous solution containing 2% stock concentration of detergent for 1 h at 80 °C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature. Applications and evaluation of fastness properties were carried out according to the standard methods in Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria.

2.2. Methods

The synthesis of the bifunctional azo reactive dyes involves four (5) steps which are cyanuration of the acids, condensation of the cyanurated acids, tetrazotisation of the intermadiates, coupling of the tetrazotised intermediates with the condensed cyanurated acids and refluxing with sulphatoethylsulphone (Oforghor et al; 2020).

2.2.1. General procedure for Tetrazotization of Intermediates

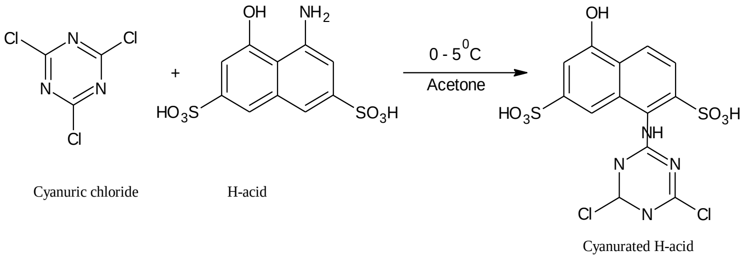
1,4-benzenediamine (0.54g, 0.005mol) was suspended in distilled water (60ml) and hydrochloric acid (0.36g) was added dropwise to the well stirred suspension. The mixture was gradually heated up to 70^{o}C, till clear solution was obtained. The formed solution was gradually cooled to below 5^{o}C in an iced bath, then already cooled (0-5^{o}C) $NaNO_2$ (0.6g in 4ml H_2O) was added over a period of 30mins with continuous stirring. The stirring was continued for one (1) hour, maintaining the temperature of 0^{o}C-5^{o}C with positive test for nitrous acid with starch iodide paper. After completely destroying the excess of nitrous acid with the required amount of sulphamic acid, the clear tetrazonium solution at 0^{o}C-5^{o}C obtained was used for next coupling reaction. The reaction as shown in the reaction scheme 1 below:



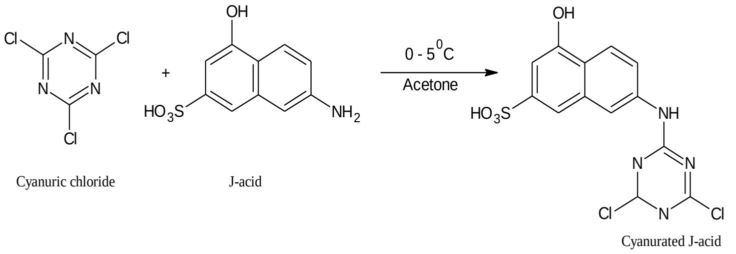
Scheme 1. Tetrazotization of 1,4’-diaminobenzene

2.2.2. General procedure for cyanuration of the acids

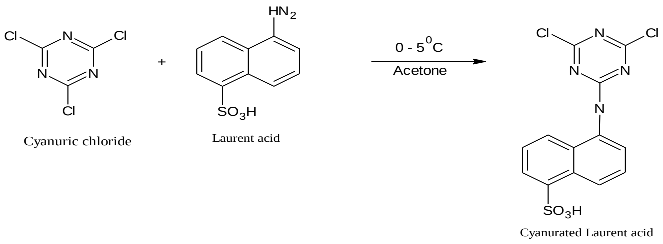
Cyanuric chloride (1.85g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19g, 0.01mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated H-acid solution was used for subsequent coupling reaction as shown in scheme 2a below. The same procedure (method) was followed to cyanurate J-acid, Laurent-acid, Tobias-acid and Gamma-acid in scheme 2b, 2c, 2d and 2e respectively as shown below.



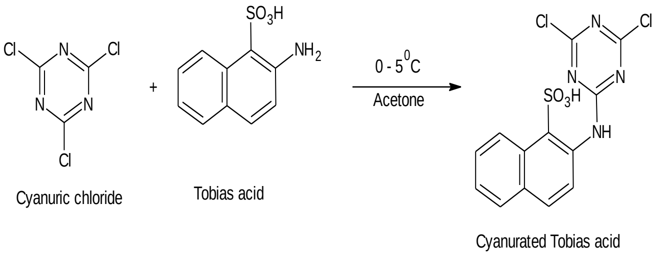
Scheme 2a. Cyanuration of H-acid



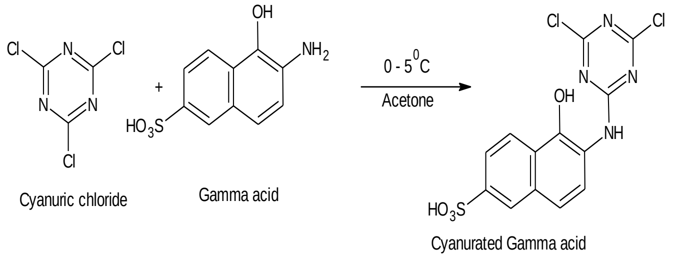
Scheme 2b. Cyanuration of J-acid



Scheme 2c. Cyanuration of Laurent acids



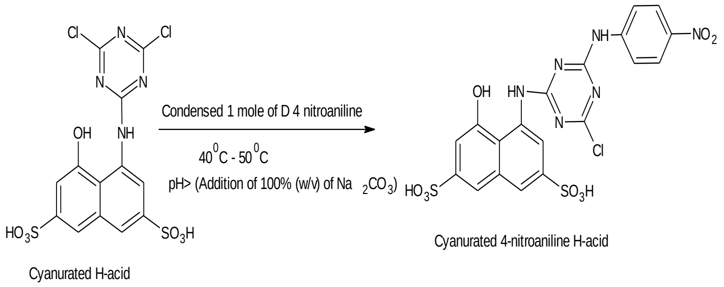
Scheme 2d. Cyanuration of Tobias acid



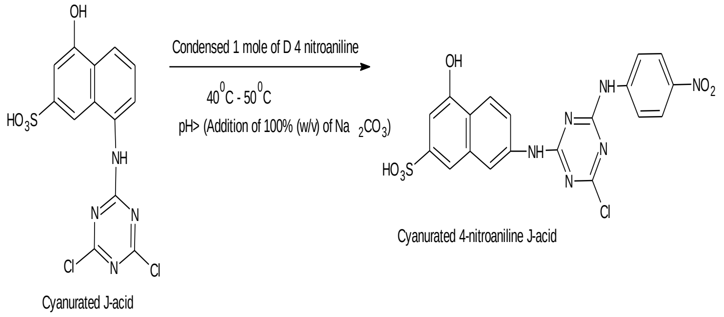
Scheme 2e. Cyanuration of Gamma-acid

2.2.3. General procedure for condensation of the cyanurated acids

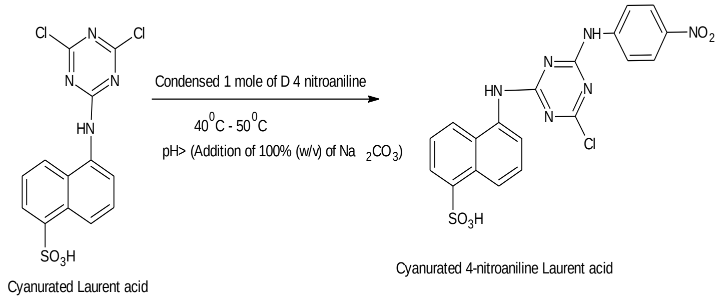
The temperature of ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 moles) was gradually raised to 45°C for half an hour. To this cyanurated H-acid, the 4-nitro aniline (1.39 g, 0.01 moles) was added slowly at same temperature, during a period of 30 min, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1%w/v). After the addition was completed, stirring was continued for further 3 hours. The cyanurated 4- nitroanilino H-acid solution thus obtained was subsequently used for further coupling reaction as shown in scheme 3a. The same procedure (method) was followed for the condensation of cyanurated in scheme 3b (J-acid), 3c (Laurent-acid), 3d (Tobias-acid) and 3e (Gamma-acid) respectively as shown below.



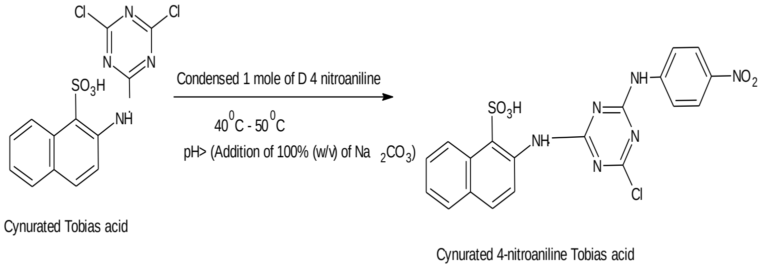
Scheme 3a. Condensation of cyanurated H-acid



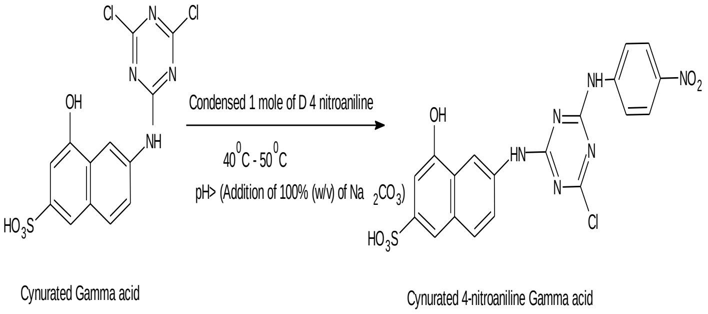
Scheme 3b. Condensation of cyanurated J-acid



Scheme 3c. Condensation of cyanurated Laurent-acid



Scheme 3d. Condensation of cyanurated Tobias-acid

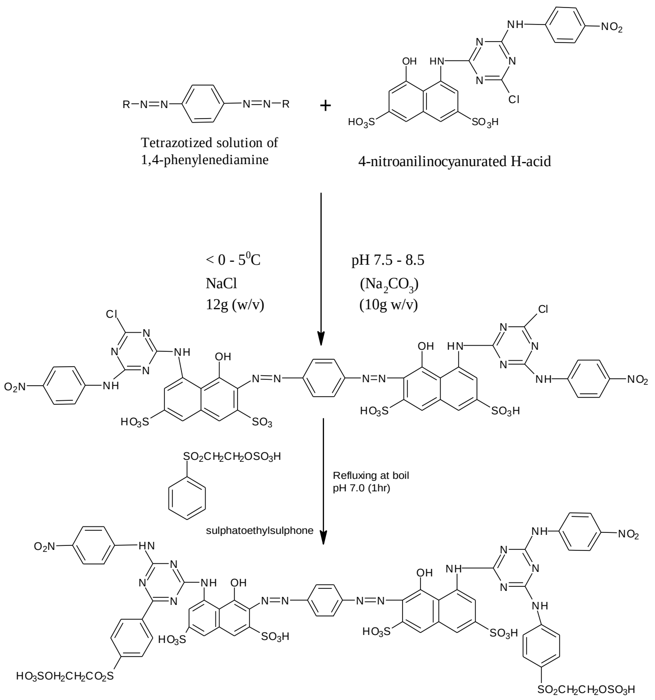


Scheme 3e. Condensation of cyanurated Gamma-acid

2.2.4. Procedure for synthesis of dyes DB_1

Dye DB_1 was synthesised by addition of the previously prepared fresh tetrazotized solution of 1,4-phenylenediamine dropwise over a period of 10 – 20 minutes to the well stirred ice-cold 4-nitroanilino cyanurated H-acid solution. There was the simultaneous addition of sodium carbonate solutions (Na_2SO_3) (10% w/v) to maintained pH 7.5 – 8.5 and stirring was continued for 3 – 4h at a constant temperature below 0 – 5^0C, then sulphatoethylsulphone (2.86g, 0.01mol) was added dropwise over 15minutes with continuous stirring and reflux at boil for 1h, then salted and stirred for further 1h. The solid precipitate was filtered, washed with little amount of acetone and dried at room temperature to give dye DB_1 as shown in scheme 4a.

Following the procedure above the other bifunctional sulphatoethylsulphone (SES) azo reactive dyes DB_2 (J-acid, 3b), DB_3 (Laurent acid, 3c), DB_4 (Tobias acid, 3d) and DB_5 (Gamma acid, 3e) as shown in Table 1.



Scheme 4a. Synthesis of dye DB_1

3.0. Dyeing of fibres

The synthesized dyes DB_1, DB_2, DB_3, DB_4 and DB_5 were applied on silk fabrics using exhaustion method and depth of shade, 2% (Oforghor et al, 2020). A mild alkaline conditions, pH 8.0-9.0 (Na_2CO_3, 0.4ml of 10%w/v) was used for the dyeing of silk fabrics while a weakly acidic conditions [(acetic acid-1,5ml of 10%w/v, NaCl-4ml of 10%w/v, distilled water-14.4ml)] was used for the dyeing of silk fabrics at 1:50 liquor-ratio for the dyeing of both fabrics

3.1. Dye Exhaustion

For all dyeing, the dye exhaustion was measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath was measured on Shimadzu UV-2401PC UV/Vis spectrophotometer at □max of the dye. The percentage of dye exhaustion (%E) was calculated using Eqn (1):

$$\% E = \left[\left(\frac{C_1 - C_2}{C_1}\right)\right] \times \frac{100}{1} \qquad (1)$$

where C_1 is the concentration of the dyebath before and C_2 is the concentration of the dyebath after dyeing (Oforghor *et al.*, 2020, Burkinshaw *et al*., 2001 and Lewis *et al.*, 2000).

3.2. Dye Fixation

The dye fixation (%F), the percentage of the exhausted dye chemically bound on the wool fabric, was measured by refluxing the wool dyed samples in 50% aqueous DMF (20:1 LR) for 15 min to extract the unfixed dye (Burkinshaw, et al., 2001). This procedure was repeated until the extract was colorless. The concentration of the extract was then measured spectrophoto-metrically at the λmax value of each dye and the dye fixation ratio calculated using Eq. 2.

$$\% F = \left[\left(\frac{C_1 - C_2 - C_3}{C_1 - C_2}\right)\right] \times \frac{100}{1} \qquad (2)$$

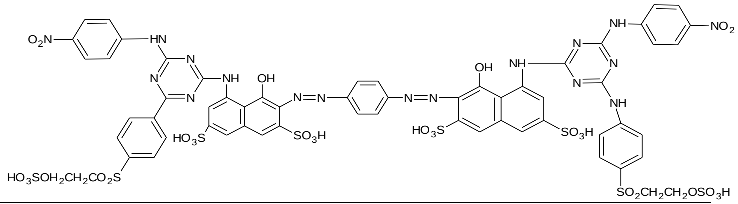
where C_3 is the concentration of extracted dye

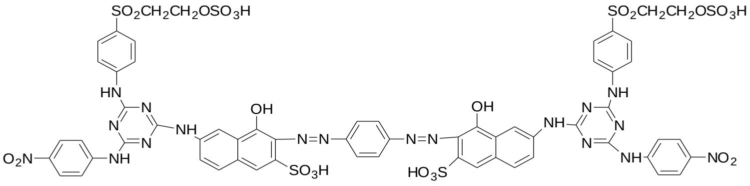
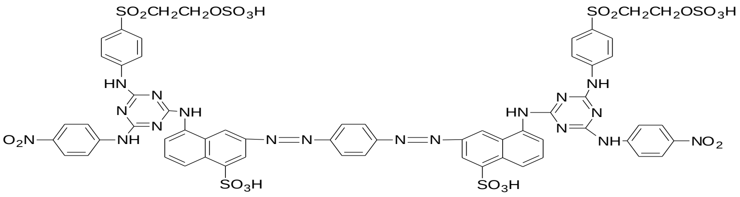
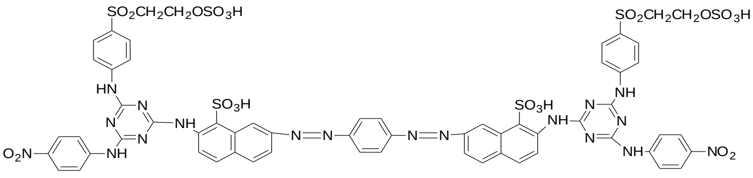
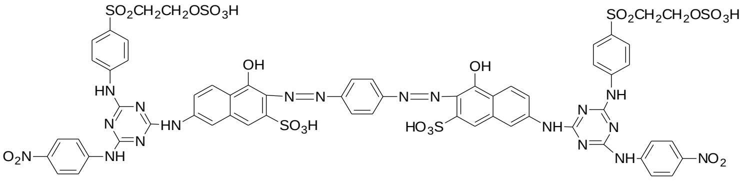
4.0. Results and Discussions

4.1. Tetrazotisation, cyanuration and condensation of the intermediates and synthesis of the bifunctional sulphatoethylsulphone (SES)

Preparation of Tetrazotised solution of 1,4-benzenediamine was done by suspending 1,4-benzenediamine and adding HCl (0.36g) dropwise with continuous stirring and the temperature raised to 70^{o}C till a clear solution is achieved. The temperature lowed to below O^{o}C-5^{o}C and a solution of already ice cold $NaNO_2$ was added in small lots over 5 minutes with continuous stirring for 1h maintaining same temperature until a clear solution is achieved as shown in scheme 1. Cyanuration of the acids as shown in Schemes 2a-2e was carried out by stirring cyanuric chloride in acetone at a temperature below 0^{o}C-5^{o}C for an hr, then a neutral solution of H-acid [in aqueous solution of $NaCO_3$ (10% w/v)} added in small lots over an hr while maintaining a constant pH by adding 1% w/v $NaCO_3$ at a temperature below 0^{o}C-5^{o}C with continuous stirring for 4h until a clear solution was obtained. In schemes 3a-3e the condensation of the cyanurated acids was carried out by raising the temperature of the ice-cold well stirred cyanurated acids [(H-acid (3a), J-acid (3b), Laurent acid (3c), Tobias acid (3d) and Gamma acid (3e)] gradually to 50^{o}C over 30 minutes, 4-nitroaniline was added in small lots over 30 minutes while maintaining a constant pH by adding 1% w/v $NaHCO_3$ with continuous stirring for 5h to obtain the 4-nitroanilino cyanurated acids. The dye DB_1(4a) was synthesised according the route shown in scheme 4a by adding freshly prepared solution of tetrazotised solution of 1,4-benzenediamine dropwise to an ice-cold well stirred of 4-nitroanilino cyanurated H-acid over a period of 10-15 minutes by maintaining pH at 7.5-8.5 by adding $NaCO_3$ (10%w/v) solution at the same time with continuous stirring for 3-4h at a temperature below 0^{o}C-5^{o}C, then sulphatoethylsulphone (2.81g, 0.01mol) was added dropwise over 15minutes with continuous stirring and reflux at boil for 1h, then salted and stirred for further 1h. The solid violet precipitate was filtered, washed with little amount of acetone and dried at room temperature. Following the procedure above the other bifunctional sulphatoethylsulphone (SES) azo reactive dyes DB_2 (4b), DB_3 (4c), DB_4 (4d) and DB_5 (4e) were synthesised using the various cyanurated coupling components such as J-acid, Laurent acid, Tobias acid and Gamma acid respectively as shown in Table 1, after which the dye was precipitated by adding 12g NaCl with continuous stirring for further 1h. The dye filtered, washed and dried at room temperature.

Table1. Structures and IUPAC names of the Synthesized bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	IUPAC Name	Structures of the Synthesized Bi- functional azo reactive Dyes
DB_1	3,3ˈ-(1,4-phenylenebis(diazene-2-1-diyl)bis(4-hydroxy-5-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2,7disulfonic acid)	

DB_2	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4-hydroxy-6-((4-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2-sulfonic acid)	
DB_3	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(5-(4-((4-nitrophenyl)amino)-6-((4-((2(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1-sulfonic acid)	
DB_4	7,7'-(1,4-phenylenebis(diazene-2,1-diyl))bis(2-((4-((4-nitrophenyl)amino)-6-((4-((2(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1-sulfonic acid)	
DB_5	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4-hydroxy-7-((4-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2-sulfonic acid)	

The physical characteristics of the synthesized dyes are shown in Table 2, which indicated that the molecular weight of all the synthesized dyes is on the high side. Oforghor et al.; (2020A) reported that high molecular weight dyes generally exhibit high melting points and this agrees with the findings since most of the synthesized dyes have high melting points. From the Table 1, the synthesized dyes recorded high percentage yields which are an indication of careful control of the experimental conditions (Mousa et al., 2014). The synthesized dyes also exhibit very high solubility which is an indication that the dyes are highly branched and the position of the functional groups in the carbon chains (Oforghor et al., 2020). The colour and/or hue of the synthesized dyes range from purple, red, pink, due to the nature and presence of functional groups such as -NH_2 and -OH on the dye moiety.

Table 2. Visible Absorption Maxima of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	Mol. Wt (g/mol)	Mt. Pt (^oC)	Yield (%)	DMF (λmax)	Water (λmax)	ε_{max} in DMF $x10^4 1Mol^{-1}cm^{-1}$
DB_1	1756.05	347-348	56	495	452	6.59
DB_2	1596.14	335-337	82	480	480	1.47
DB_3	1564.15	325-327	69	461	461	3.27
DB_4	1564.15	315-318	74	495	495	1.82

DB_5	1596.14	320-322	78	526	526	9.47

The visible absorption spectroscopic properties of the dyes were recorded in DMF and water. From the data reported in Table 2, it is apparent that the λ_{max} value depends on the coupling components used. The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituent. The shift in λ_{max} of the synthesized bifunctional azo reactive dyes in different solvents (solvatochromism) is as a result of the solvatochromic effects emanating from changes in dielectric constant of the solvent. The measuremrnt of λ_{max} in DMF and water indicated that λ_{max} of the intermolecular charge transfer bonds exhibit a remarkable red shift on transfer from non-polar to polar solvent. This behaviour can be attributed to the polar excited states of the synthesised bifunctional azo reactive dyes are stabilized by polarization interactions forces as the polarisability of the solvent increases (Oforghor et al; 2020). The visible absorption maxima of the synthesised bifunctional azo reactive dyes fall within the visible region (400-700nm) of the electromagnetic spectrum which showed that the synthesised bifunctional azo reactive dyes are colourants with high commercial integrity. The values of the molar extinction coefficient (ε) that were determined by Beer-Lambert's law are in the range of 14705.12-94704.13mol^{-1}cm^{-1} which is an indication of high absorption intensity of the synthesised bifunctional azo reactive dyes in DMF respectively. However, the synthesised bifunctional azo reactive dyes have the same chromophoric functionalities, but different in the bridging groups. The presence of electron donating or electron attracting (withdrawing) groups at the suitable position of the coupler ring affects the absorption characteristics of the synthesised bifunctional azo reactive dyes. Meanwhile, comparing the λmax of the synthesised bifunctional azo reactive dyes DB_1, DB_2, DB_3, DB_4 and DB_5 in DMF showed that their nature of their coupling components (cyanurated 4-nitroanilino H-acid, cyanurated 4-nitroanilino J-acid, cyanurated 4-nitroanilino Laurent-acid, cyanurated 4-nitroanilino Tobias-acid and cyanurated 4-nitroanilino Gamma-acid) are very significant in the context of colour change (Patel et al; 2012). However, dye DB_1 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino H-acid and refluxing with sulphatoethylsulphone which absorbed at 495nm while DB_2 which is obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino J-acid and refluxing with sulphatoethylsulphone which absorbed at 480nm, in the same solvent hence there was a hypsochromic shift of 15nm. This is attributed to the introduction of additional donor groups onto the coupling component. Dye DB_3 was obtained by tetrazotising 1,4-benzenediamine and coupling with cyanurated 4-nitroanilino Laurent acid and refluxing with sulphatoethylsulphone which absorbed at 461nm, dye DB_3 shifted hypsochromically by 34nm and 24nm when compared with DB_1 and DB_2 respectively. When cyanurated 4-nitroanilino Tobias acid was employed as the coupling component and couple with a solution of tetrazotising 1,4 benzenediamine and refluxing with sulphatoethylsulphone, dye DB_4 which absorbed at 495nm. Comparing dye DB_4 with dye DB_1, DB_2 and DB_3, there was 0nm shift for DB_1, 15nm bathochromic shift for DB_2 and 34nm bathochromic shift for DB_3 respectively. Dye DB_5 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Gamma acid and refluxing with sulphatoethylsulphone which absorbed at 526nm, comparing dye DB_5 with dye DB_1, DB_2 , DB_3, and DB_4, all the dyes shifted bathochromically 31nm for DB1, 40nm for DB2, 45nm for DB3 and 31nm for DB4 respectively. All the shifts experienced are as a result of introduction of electron donating groups or electron withdrawing groups in the dye moiety.

Table 3. FT- IR of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	Mol. Formula	Mol. Wt	Yield (%)	Melting Point	FT-IR cm^{-1}
DB$_1$	$C_{60}H_{49}N_{18}O_{30}S_8$	1756	56	347-348	3501 (O-H str. vibr.), 3441 (N-H str vibr.), 3070 (C-H str vibr.), 1550 (N=N str vibr.), 1420 (C-N str vibr.), 1650 (N-H bend. vibr.), 1021 (S=O str vibr.), 1325 (N=O str vibr.), 841 (SO_3H str vibr.)
DB$_2$	$C_{60}H_{48}N_{18}O_{24}S_6$	1596	82	335-337	3439 (O-H str vibr.), 3371 (N-H str vibr.), 3073 (C-H str vibr.), 1597 (N=N str vibr.), 1366 (C-N str vibr.), 1600 (N-H bend. vibr.), 1046 (S=O str vibr.), 1301 (N=O str vibr.), 835 (SO_3H str vibr.)
DB$_3$	$C_{60}H_{48}N_{18}O_{22}S_6$	1564	69	325-327	3398 (O-H/N-H str vibr.), 2955(C-H str vibr.), 1597(N=N str vibr.), 1498 (C-N str vibr.), 1650 (N-H bend. vibr.), 1229 (S=O str vibr.), 1329 (N=O str vibr.), 851 (SO_3H str vibr.)
DB$_4$	$C_{60}H_{48}N_{18}O_{22}S_6$	1564	74	316-318	3442 (O-H/N-H str vibr.), 2919 (C-H str vibr.), 1329 (N=N str vibr.), 1460 (C-N str vibr.), 1597 (N-H bend. vibr.), 1134 (S=O str vibr.), 1304 (N=O str vibr.), 828 (SO_3H str vibr.)
DB$_5$	$C_{60}H_{48}N_{18}O_{24}S_6$	1596	78	320-322	3395 (O-H str vibr.), 3325 (N-H str vibr.), 3026-2990 (C-H str vibr.), 1595 (N=N str vibr.), 1420 (C-N str vibr.), 1605 (N-H bend. vibr.), 1025 (S=O str vibr.), 1335 (N=O str vibr.), 848-840 (SO_3H str vibr.)

The Infra-red Spectral of all the synthesised dyes DB$_1$, - DB$_5$ revealed that O-H and N-H showed stretching vibration at 3561cm-^{1}-3371 cm-^{1}, C=H showed stretching vibration at 2955cm-^{1}, C-N showed stretching vibration at 1574cm-^{1}, 1305cm-^{1}, 1464cm-^{1}, N=N showed stretching vibration at 1597cm-^{1}, S=O showed stretching vibration at 1150cm-^{1}, 1060cm-^{1} (asym. And sym), N=O showed stretching vibration at 1495cm-^{1}, 1411cm-^{1}, 1335cm-^{1}, C-Cl showed stretching vibration at 784cm-^{1} and SO_3H showed stretching vibration at 841cm-^{1} respectively as showed in Table 3.

Table 4. ^{1}HNMR of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	**^{1}HNMR**
DB$_1$	3.64 (2H, S, α –CH$_2$), 3.81 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH$_2$), 4.64 (2H, S, –OH), 7.06 – 8.34 (38H, m, Ar –H), 8.60 (1H, S, SO$_3$H)
DB$_2$	3.63 (2H, S, α –CH$_2$), 3.81 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH$_2$), 4.64 (2H, S, –OH), 7.06 – 8.34 (37H, m, Ar –H), 8.60 (1H, S, SO$_3$H)
DB$_3$	3.63 (2H, S, α –CH$_2$), 3.66 (4H, S, –NH), 3.91 – 3.93 (2H, S, β –CH$_2$), 7.06 – 8.34 (39H, m, Ar –H), 8.60 (1H, S, SO$_3$H)
DB$_4$	3.63 (2H, S, α –CH$_2$), 3.65 (4H, S, –NH), 3.91 – 3.93 (2H, S, β –CH$_2$), 7.06 – 8.34 (39H, m, Ar –H), 8.60 (1H, S, SO$_3$H)
DB$_5$	3.63 (2H, S, α –CH$_2$), 3.66 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH$_2$), 4.84 (2H, S, –OH), 7.06 – 8.34 (37H, m, Ar –H), 8.60 (1H, S, SO$_3$H)

The ^{1}H-NMR spectral of the dyes showed signals (singlet) at 3.64 δ ppm which confirmed the presence of methylene (–CH) protons, 4.84 δ ppm due to the presence of hydroxyl groups (–OH), 3.92-3.94 δ ppm confirmed the presence of methylene (-CH$_2$) protons, 3.64 δ ppm which confirmed the presence of amino (-NH$_2$) protons, 7.06-8.34 δ ppm due to the presence of aromatic (Ar-H) protons, 8.60 δ ppm because of the presence of sulphonate (-SO$_3$H) groups.

Table 5. Mass Spectroscopy data for bifunctional sulpathoethylsulphone azo reactive dyes DB$_1$ – DB$_{20}$

Dye No.	**Empirical formula**	**Experimental values of m/z fragment**	**Corresponding positive charge fragment**	**Theoretical value**
DB$_1$	$C_{60}H_{49}N_{18}O_{30}S_8$	46.0, 76.0, 107.2, 318.1, 374.0, 1757.2	NO_2^+, $C_6H_4^+$, $C_6H_8N_2^+$, $C_7H_6N_3O_2S_2^+$, M	1757
DB$_2$	$C_{60}H_{48}N_{18}O_{24}S_6$	46.0, 76.0, 108.1, 239.1, 373.0, 1596.1	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1596
DB$_3$	$C_{60}H_{48}N_{18}O_{22}S_6$	46.0, 76.0, 108.2, 222.1, 374.1, 1564.3	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_4NO_3S^+$, M	1564
DB$_4$	$C_{60}H_{48}N_{18}O_{22}S_6$	46.0, 76.0, 107.1, 223.2, 374.3, 1564.2	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_3S^+$, M	1564

DB_5	$C_{60}H_{48}N_{18}O_{24}S_6$	46.0, 76.0, 107.3, 240.2, 374.1, 1596.2	NO_2, C_6H_4, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1596

The mass spectrum MS for dye DB_1 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S_2^+$, $C_6H_8N_2^+$, $C_{10}H_8NO_7S_2^+$, which indicates molar masses of 46.0, 76.0, 107.2, 318.1, 374.0 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1757.2 g/mol and this is in agreement with the molecular mass 1756.1 g/mol of the synthesised dye DB_1. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye DB_2 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 108.1, 239.1, 373.0 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1596.1 g/mol and this is in agreement with the molecular mass 1596.1 g/mol of the synthesised dye DB_2. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye DB_3 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_4NO_3S^+$, which indicates molar masses of 46.0, 76.0, 108.2, 222.1, 374.1 g/mol respectively. The mass spectrum showed a molecular ion (M+) at m/z 1564.3 g/mol and this is in agreement with the molecular mass 1564.2 g/mol of the synthesised dye DB_3. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye DB_5 analysis revealed a fragmentation pattern of NO_2, C_6H_4, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 107.3, 240.2, 374.1 g/mol respectively. The mass spectrum showed a molecular ion (M+) at m/z 1596.2 g/mol$^-$and this is in agreement with the molecular mass 1596.1 g/mol of the synthesised dye DB_5. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems.

Table 6. Exhaustion and fixation study of the synthesised azo reactive dyes on silk fabric

		Exhaustion (%)	**Fixation (%)**
Dye No	**Shade on silk fabric**	**silk fabric**	**Silk fabric**
DB_1	Brown	85	72
DB_2	Orange	65	70
DB_3	Yellow	72	85
DB_4	Orange	65	65
DB_5	Yellow	62	72

The percentage exhaustion of 2% dyeing on silk fabric showed from 62% to 85%, where dye DB_1 gives maximum exhaustion of 85% and minimum exhaustion of 62%. The percentage fixation of 2% dyeing on silk fabric showed from 65% to 85 %, where dye DB_3 give a maximum fixation of 85% and minimum fixation of 65%. The details on the results of percentage exhaustion and fixation are showed in Table 4.

Table 7. Fastness performance properties of the synthesised azo reactive dyes on wool fabrics

			Perspiration fastness	
Dye No	**Wash fastness**	**Light fastness**	**Alkaline**	**Acidic**
	Silk	**silk**	**silk**	**silk**
	cc	cc	cc	cc
DB_1	4	5-6	3-4	4
DB_2	4-5	5-6	3-4	3-4
DB_3	4-5	4	3-4	4
DB_4	4	4-4	3-4	4
DB_5	4-5	5	3-4	3-4

cc=colour change

Fastness properties to washing: 1-poor, 2-moderate, 3-fair, 4-very good, 5-excellent;

Fastness properties to light: 1-poor, 2-slight, 3- moderate, 4- fair, 5- good, 6- very good;

Fastness properties to perspiration – alkaline and acidic: 1-poor, 2-fair 3-good, 4-very good.

The results for the fastness properties to washing (IS 765-1979 (Patel et al, 2011), fastness properties to light (BS: 1006-1978 (Patel et al, 2011) and fastness properties to perspiration – alkaline and acidic (Oforghor et al, 2020A and Kkaeaei et al, 2013) are recorded in Table 4. From the result the synthesised dyes showed satisfactory performances to fastness properties to washing (between 4-5), fastness properties to light (between 4, 4-5, 6) and fastness properties to perspiration – alkaline and acidic (between 3-4, 4). This is an indication of good dye penetration and excellent affinity, cross linking between the dye and the fibre.

5.0. Conclusion

Bifunctional Sulphatoethylsulphone (SES) azo reactive dyes were synthesised with 4- nitroanilino cyanurated acids- (cyanurated 4-nitroanilino H-acid, cyanurated 4-nitroanilino J-acid, cyanurated 4-nitroanilino Laurent-acid, cyanurated 4-nitroanilino Tobias-acid and cyanurated 4-nitroanilino Gamma-acid) as coupling components and reacting with tetrazotised solution of 1,4-benzenediamine. However, the visible absorption spectra of the dyes showed maximum absorption (λ_{max}) in the range of 400-700nm. The dyes recorded brown, purple, orange and yellow colours on silk fabrics. The difference in colour of the dyes may be attributed to both the nature and position of the substituent. The dyes gave a satisfactory performance of exhaustion and fixation efficiency on silk fabrics. The fastness properties to washing, fastness properties to light and fastness properties to perspiration – alkaline and acidic of the dyes on silk fabrics showed good to excellent performance.

Declarations

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Competing Interests Statement

Authors have declared no competing interests.

Consent for Publication

The authors declare that they consented to the publication of this study.

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