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Synthesis, stability and printing properties of a novel 2-sulphophenoxy-4-chloro-s-triazine reactive dye for Inkjet Printing of Wool

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Abstract

We report here the synthesis and characterisation of new a medium-reactivity reactive dye containing 2-sulphophenoxy-4-chloro-s-triazine, having enhanced the activity of the chlorine atom for further substitution by the functional groups carried by wool fibre. In addition, a dichloro-s-triazine dye was also synthesised for the purpose of comparison. The progress of synthesis reactions and purity of the dyes were determined using capillary electrophoresis and thin layer chromatography. The molecular structure and the chemical compositions of the synthesised dyes were confirmed using Fourier transform-infrared spectral data and elemental analyses. The inks containing the synthesised dyes were formulated and inkjet-printed onto wool fabrics and the printed fabrics were steamed at 102 °C. Compared to the dichloro-s-triazine dye, superior performance in terms of ink stability, colour strength and dye fixation were observed for the new 2-sulphophenoxy-4-chloro-s-triazine dye. In addition, the light fastness of the fabric printed with the inks containing the new dye was 0.5 grade greater than that of the fabric printed with the inks containing the dichloro-s-triazine dye and no change in shade and staining were observed following wash fastness tests of the fabrics printed with the inks containing the new dye.

Key Terms

Wool, Inkjet Printing, Reactive Ink, Ink Stability, Sulphophenoxy

1 INTRODUCTION

Inkjet printing of textiles contains a number of potential benefits over traditional screen printing methods by offering much greater design possibilities with respect to repeat size and colour range.[1,2] Inkjet printing eliminates the set up cost associated with screen preparation and can enable cost effective short run production. It allows the creation of visual effects such as tonal gradients and infinite pattern repeat size that cannot be practically achieved by screen printing technology.[3] Inkjet printing is recognised as the best available textile printing technique and is a simple and environmentally clean technology.[1,4] However, inkjet printing also has its disadvantages such as its relatively lower productivity, slightly more demanding machine maintenance and limitations in available dye selection.

The past decade has seen significant research activities in the development of inks for textile inkjet printing.[5,6,7,8,9] To obtain a good printing quality, the ink has to satisfy certain criteria such as extremely low salt content, high purity, non-corrosiveness, surface tension in the range of 25–65 dynes.cm^{-1}, high light and wash fastness, thermal and chemical stability, low viscosity, excellent storage stability and high solubility.[1,10,11] These properties also need to remain consistent for a prolonged period of time to prevent dye precipitation in the ink cartridge and hence blockage of the cartridge nozzles. To date, development of ink formulations having the required rheology, high stability, high fixation properties and excellent colour fastness for textile printing has continued to attract research attention.

Reactive dyes are being printed on wool and silk, in addition to the already well-known fields of application on cellulose and cellulose/polyester fabrics. [12,13,14] Reactive dyes offer advantages of excellent fastness against repeated washing and brilliance of shade in comparison with appropriately chosen acid and chrome dyes accompanied by the simpler dyeing methods compared with chrome dyes. In addition, reactive dyes are becoming increasingly important in wool coloration due to environmental pressures on the use of chrome and pre-metallised dyes.[1,15] Furthermore, inkjet printing provides a favourable method for wool printing because of the ability to produce economical short print runs[1,13,16] and providing flexibility in print design.[17,18]

Reactive dyes are normally preferred, for inkjet printing, over other water soluble dyes due to their excellent colour fastness and brilliance in shade, once fixed to the fibres. [11,13] Reactive inks (inks based on reactive dyes) from major suppliers are typically based on monochloro-s-triazine and vinylsulphone dyes.[5,6,19] These inks are based on low reactivity dyes and cover the majority of the inkjet market,[13,20] whilst, volume of usage wise, monochloro-s-triazine based inks are the market leaders.[20,21,22,23,24,25,26] These inks show excellent stability but fairly limited dye fixation under inkjet printing and post-printing processing conditions.[27,28] Moreover, in order to achieve the necessary high level of wash fastness, the unfixed or hydrolysed dye must be removed effectively. For this reason, energy intensive washing-off procedures are required (e.g. a cycle consisting of cold, hot, warm and cold washes).[29] Another common problem with reactive inks, especially based on high reactivity dyes, is the susceptibility of reactive groups to hydrolysis.[1,13,30] If the reactive group is hydrolysed during ink storage, the dye will not effectively fix to the substrate and thus will not give optimal fixation. Furthermore, due to high susceptibility toward hydrolysis reactive inks show limited shelf life.[30]

A comprehensive review of dyes for inkjet printing has been provided by Fryberg.[31] According to Fryberg, dyes with sulpho groups, having high solubility, are well suited for ink formulations. Gisler[32] prepared trisazo reactive dye based on fluoropyrimidine reactive group claiming their suitability in inkjet printing of hydroxyl group and amino group containing fibres. Eltz and Russ[33] prepared a series of reactive dyes of increased stability by modification of commercially available dyes with cyanamide and claimed that they are surprisingly stable against hydrolysis and particularly suitable for inkjet printing. Clark *et al.*[34] prepared reactive dyes through modification of commercial Drimarene K dyes with p-sulphophenoxy and claimed that the modified dye based ink showed excellent solubility and stability during storage for up to one year. Maheshwari[35] prepared a yellow reactive dye of increased water solubility by modification of Reactive Yellow 160 with secondary amines having sulphonate or carboxylate groups. It was claimed that this dye, when used in inkjet printing of cotton and wool, exhibited good levels of fixation and therefore requiring minimal washing-off. More recently, Yang *et al.*[18] prepared di-substituted phenol sulphonic reactive dyes having high stability in buffered ink.

In light of these findings, we report here the synthesis, characterisation and fixation values of a new medium-reactivity reactive dye (yellow 2-sulphophenoxy-4-chloro-s-triazine), containing electron-donating phenoxy group in the triazine reactive group which increases the electron density of the triazine ring, thus decreasing the reactivity of the ring for further substitution reactions. It was expected that the 2-sulphophenoxy-4-chloro-s-triazine dye should exhibit superior performance in terms of stability in water-based inkjet formulations, dye fixation, colour strength and fastness properties when applied onto 100% wool fabric by inkjet printing. A yellow dichloro-s-triazine dye was also synthesised for comparison.

2 EXPERIMENTAL

2.1 Materials

7-amino-1,3-naphthalenedisulphonic acid (88%), sodium nitrite (98%), *m*-toluidine (99%), cyanuric chloride (99%), sodium 4-hydroxybenzenesulphonate dihydrate (98%), sodium metabisulphite, carboxymethyl cellulose (CMC), polysorbate 20 and N-methylmorpholine N-oxide (NMMO) were supplied by Sigma-Aldrich and used as received. Urea (MP Biomedicals), Alcopol O 60 (Acros organics), 2-pyrrolidone (Acros organics), 2-propanol (Fisher), Sandozin NIE (Clariant) were also purchased and used as received.

Commercially available worsted 100% wool fabric, 1:1 twill, untreated, 200 g/m^2, kindly supplied by Woolmark Company (UK), was used for this study.

2.2 Synthesis of Yellow 7-[(4-Amino-2-methylphenyl)azo]-1,3-Naphthalenedisulfonic-acid Dye (1)

2.2.1 Diazotization

The synthesis routes to prepare the reactive dyes used in this study are shown in Scheme 1. Thus, 7-amino-1,3-naphthalenedisulphonic acid (17.22 g, 0.05 mol, 88%) was suspended in water (100 cm^3) and then treated with concentrated hydrochloric acid (10 cm^3, 0.125 mol, 36.6% *w/v*) and cooled to 20 °C. The temperature of the reaction mixture was lowered to 0 to 5 °C by adding ice, and diazotization was carried out by adding 1N sodium nitrite solution (3.52 g, 0.05 mol, 98%). The reaction mixture was stirred at 0 to 5 °C and pH < 2. Diazotization was deemed complete as soon as a small amount withdrawn from a reaction mixture did not give a yellow colour when treated with 2N sodium acetate solution. Excess nitrous acid was removed from the reaction mixture by adding sulphamic acid (confirmed by spotting a drop of reaction mixture on starch iodide paper).

2.2.2 Coupling

Meta-toluidine (5.40 g, 0.05 mol, 99%) was dissolved in concentrated hydrochloric acid (5 cm^3, strength 36.6%) and water (75 cm^3) and then added drop wise with good stirring into the diazo solution (0.05 mol) at 0 to 5 °C over 45 minutes. The pH of the reaction mixture was then adjusted to pH 3.5 to 3.7 by the addition of 2N sodium acetate solution and the reaction mixture was stirred for a further 4 hours at 0 to 5 °C. Solid sodium chloride was added to give a final concentration of 8% *w/v* to a stirred reaction mixture to precipitate the dye chromophore which was subsequently collected by filtration, washed with 200 cm^3 of sodium chloride solution (10% *w/v*) and dried *in vacuo*. Purification of the crude yellow chromophore **1** using solvent-nonsolvent technique (DMF–acetone, 1:2 *v/v*) yielded pure yellow chromophore 1 (18.62 g, 40.0 mmol, yield 80%) as reddish yellow powder.

Analytics: MEKC MT (4.55 min); Purity (100%); R_f (0.63); chromophore **1** structure was confirmed by FT-IR[36] (FT-IR spectrum not shown here): N–H stretch, primary amine, 3328 cm^{-1} and 3227 cm^{-1}; overtone or combinational bands, 2000–1667 cm^{-1}; C=C stretch, 1651, 1588 cm^{-1}; N–H bending, 1625 cm^{-1};C=C ring stretch, 1555, 1492; azo group stretch, 1414 cm^{-1}; C–N stretch (primary amine), 1247 cm^{-1}; sulphonate salts, 1176 cm^{-1}; in-plane C–H bend, 1037 cm^{-1}; broad, N–H wag, 881 cm^{-1}; out of plane aromatic C–H bend, 809, 763 cm^{-1}; CH_3 rock, 727 cm^{-1}.[37,38,39,40] Elemental analysis, found: C, 41.98%; H, 3.03 %; N, 8.59%; calculated for $C_{17}H_{13}N_3Na_2O_6S_2$. H_2O: C, 42.23%; H, 3.13%; N, 8.70%. The results are adjusted due to the presence of water of crystallisation. Further disagreement could be attributed to the presence of traces of salt.

2.3 Synthesis of Yellow 7-[(2,4-Dichloro-1,3,5-triazin-6-yl)amino-2-methylphenyl]azo]-1,3-Naphthalenedisulphonic-acid Dye (1a)

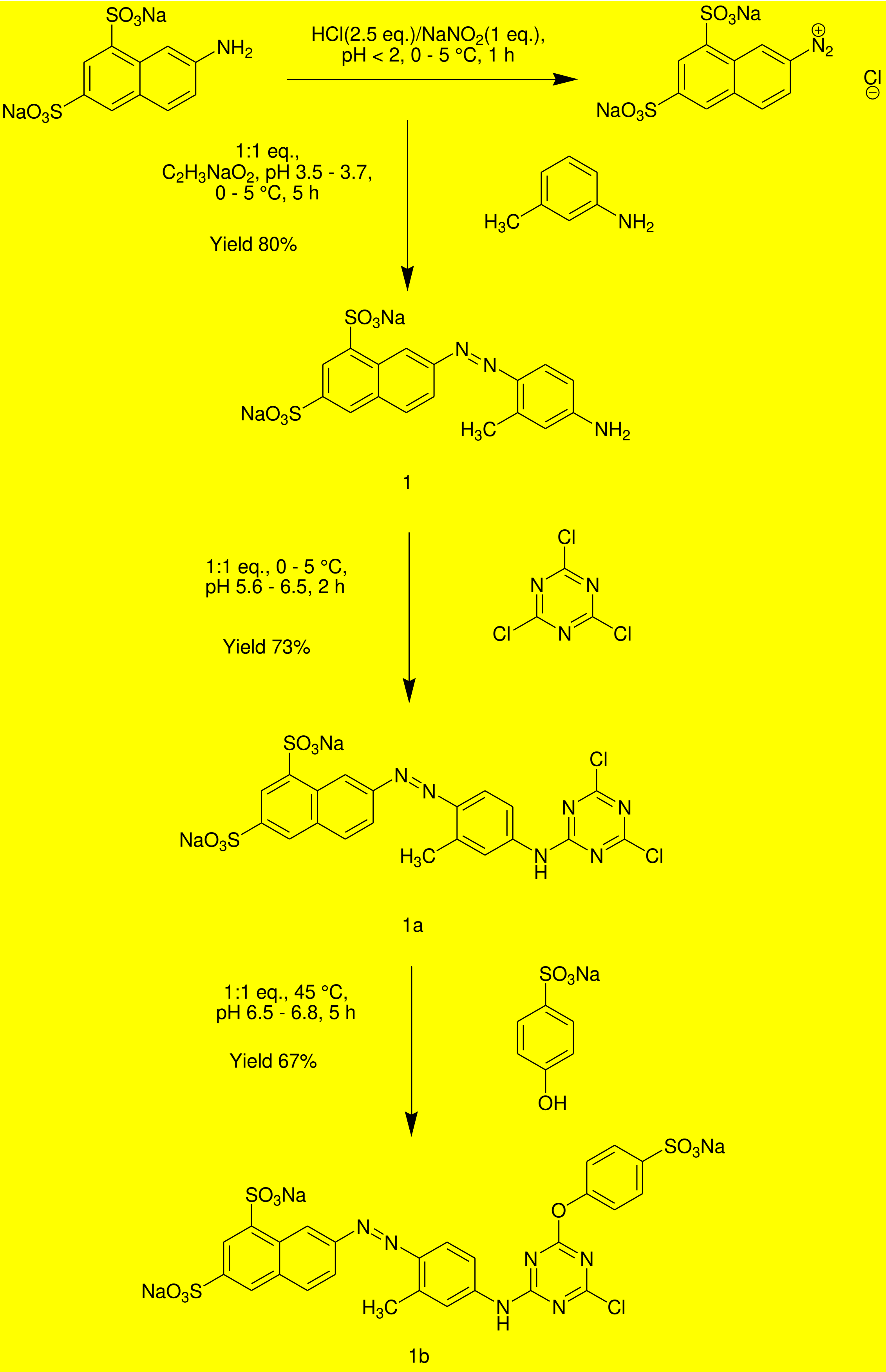
A solution of cyanuric chloride (9.22 g, 0.05 mol) in acetone (50 cm^3) was poured into a stirred mixture of water (125 cm^3) and ice (125 cm^3) at a temperature below 5 °C. Yellow chromophore **1** (0.05 M, 23.37 g) was dissolved in water (250 cm^3) and the pH was adjusted to 7.0 by the addition of 2N sodium carbonate solution which was then added drop-wise to the aforementioned cyanuric chloride solution over 30 minutes. The pH of the reaction mixture was maintained at 5.6 to 6.5 by the addition of 2N sodium carbonate solution, while the temperature was kept at 0 to 5 °C. Once the addition of the yellow chromophore **1** solution was completed, the reaction was stirred for a further 2 hours at 0 to 5 °C. When the reaction had reached to completion, the 2N sodium carbonate solution was added to the reaction mixture to raise the pH to 7.0. Phosphate buffer (30 cm^3, NaH_2PO_4 0.12 M, Na_2HPO_4 0.2 M, pH 6.4) was added to buffer the reaction mixture. The dye **1a** was precipitated by the addition of solid sodium chloride to give a final concentration of 10% *w/v*. The crude dye **1a** was collected by filtration and the filter cake was washed with 100 cm^3 of sodium chloride solution (10% *w/v*) and dried *in vacuo*. Purification of crude dye using solvent–nonsolvent technique (DMF–acetone, 1:2 *v/v*) yielded the pure dye **1a** (9.98 g, 14.6 mmol, yield 73%) as yellow powder.

Analytics: The detailed analysis of dye **1a** FT-IR spectrum is as follows; [37,38,39,40] N–H stretch, 3406 cm^{-1}; overtone or combinational bands, 2000–1667 cm^{-1}; N–H bending, 1625 cm^{-1}; C=C ring stretch, 1601, 1494 cm^{-1}; azo group stretch, 1450 cm^{-1}; C=N stretch, 1542 cm^{-1}, 1386 cm^{-1}; C–N stretch (secondary amine),1315 cm^{-1}; sulphonate salts, 1187 cm^{-1}; C–Cl stretch, 1097 cm^{-1}, 791 cm^{-1}; in-plane C–H bend, 1040 cm^{-1}; out of plane aromatic C–H bend, 751 cm^{-1}; CH_3 rock 726 cm^{-1}. Elemental Analysis: Found: C, 39.16%; H, 1.97%; N, 13.70%; calculated for $C_{20}H_{12}Cl_2N_6Na_2O_6S_2.H_2O$: C, 38.04%; H, 2.24%; N, 13.32%. MEKC MT (5.43 min); R_f (0.70); Purity (100%).

2.4 Synthesis of Yellow 7-[(2-(4-sulphophenoxy)- 4-chloro-1,3,5-triazin-6-yl)amino-2-methylphenyl]azo]-1,3-Naphthalenedisulphonic-acid Dye (1b)

Dye **1a** (6.51 g, 0.01 mol, 1 eq.) and sodium bicarbonate (1.23 g, 0.015 mol, 1.5 eq.) were dissolved in water (50 cm^3) at 45 °C. A solution of sodium 4-hydroxy benzenesulphonate (2.32 g, 0.01 mol, 1 eq.) in water (20 cm^3) was added drop wise over 15 minutes to the dye **1a** solution; the pH was maintained at 6.5 to 6.8 by the addition of saturated sodium carbonate solution. Once the addition of sodium 4-hydroxy benzenesulphonate solution was complete, the reaction mixture was stirred for a further 5 hours (until the pH value stabilised) at 45 °C.

Then solid sodium chloride to give final concentration of 10% *w/v* was added to precipitate out the dye. The crude dye **1b** was collected by filtration and the filter cake was dried *in vacuo*. Purification of the crude dye **1b** using solvent-nonsolvent technique (DMF−Acetone, 1:2 *v/v*) afforded pure dye **1b** (5.45 g, 6.72 mmol, yield 67%) as yellow powder.


SO3Na
NH2
NaO3S
HCl(2.5 eq.)/NaNO2(1 eq.),
pH < 2, 0 - 5 °C, 1 h
SO3Na
N2 ⊕
NaO3S
Cl ⊖
1:1 eq.,
C2H3NaO2, pH 3.5 - 3.7,
0 - 5 °C, 5 h
Yield 80%
H3C
NH2
SO3Na
N
N
NaO3S
H3C
NH2
1
1:1 eq., 0 - 5 °C,
pH 5.6 - 6.5, 2 h
Yield 73%
Cl
N
N
Cl
N
Cl
SO3Na
N
N
Cl
N
N
NaO3S
H3C
N
H
N
Cl
1a
1:1 eq., 45 °C,
pH 6.5 - 6.8, 5 h
Yield 67%
SO3Na
OH
SO3Na
O
SO3Na
N
N
N
N
NaO3S
H3C
N
H
N
Cl
1b

1b

SCHEME 1 Synthesis route for Yellow chromophore **1**, dichloro-s-triazine dye **1a** and 2-sulphophenoxy-4-chloro-s-triazine dye **1b**

Analytics: The detailed analysis of dye **1b** FT-IR spectrum is as follows; [37,38,39,40] N–H stretch, 3426 cm^{-1}; overtone or combinational bands, 2000–1667 cm^{-1}; C=C ring stretch, 1594, 1495, 1404 cm^{-1}; azo group stretch, 1431 cm^{-1}; triazine stretch, 1547 cm^{-1}, 1359 cm^{-1}; C–N stretch (secondary amine), 1295 cm^{-1}; sulphonate salts, 1176 cm^{-1}; C–O–C stretch, 1120 cm^{-1}; in-plane C–H bend, 1032, 1009 cm^{-1}; C–Cl stretch, 797 cm^{-1}; out of plane aromatic C–H bend, 760 cm^{-1}. Elemental Analysis: Found: C, 35.58%; H, 3.10%; N, 8.87%; calculated for $C_{26}H_{16}ClN_6Na_3O_{10}S_3.6H_2O$: C, 35.46%; H, 3.20%; N, 9.54%. The results were adjusted due to the presence of water of crystallisation in the dye molecule. Further disagreement could be attributed to the presence of traces of salt. MEKC MT (4.42 min); R_f (0.67); Purity (100%).

2.5 Procedures

The progress of synthesis reactions and purity of the dyes were monitored using Capillary Electrophoresis (Beckman Coulter P/ACE MDQ) and thin layer chromatography (TLC). The conditions used for CE (MEKC) were: buffer (20 mM sodium tetraborate, 50 mM sodium dodecyl sulphate), pH 9.3; pressure injection 0.5 psi for 10 s; voltage 25 kV; detection at 420 nm, whereas, for TLC the eluent was n-butanol−iso-propanol−ethyl acetate−water (2:4:1:3 v/v). Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer (Perkin Elmer, UK) using the PE Diamond Golden Gate sampling attachment for attenuated total reflection (ATR) measurement. Each spectrum was acquired using the following settings: 4 cm^{-1} resolution, 100 scans per spectrum and a scan speed of 0.5 cm/s. The raw data were analysed using OriginPro 9.0.0. Elemental analysis of synthesised dyes for carbon, hydrogen and nitrogen was performed using a FlashEA 1112 analyser from Thermo Scientific.[36]

2.6 Application of the Dyes

2.6.1 Ink Preparation

The inks were formulated using following composition in deionised water: 40 $g.dm^{-3}$ of synthesised yellow dyes **1a** or **1b**, 20 $g.dm^{-3}$ of 2-pyrrolidone, 300 $g.dm^{-3}$ of N-methylmorpholine N-oxide, 25 $g.dm^{-3}$ of propan-2-ol and 10 $g.dm^{-3}$ of polysorbate 20. The formulated inks were placed inside an ultrasonic-water bath for 10 min and then filtered using a 1 µm filter prior to use.[17,36]

2.6.2 Fabric Pretreatment

Wool fabric was padded at 100% wet pick-up using a Werner Mathis HVF padder with the pretreatment liquor containing 20 $g.dm^{-3}$ sodium metabisulphite[34] (diffusion accelerator), 20 $g.dm^{-3}$ CMC (thickening agent), 300 $g.dm^{-3}$ urea (humectant) and 5 $g.dm^{-3}$ Alcopol O 60 (wetting agent) (pH 7.5–8);[34,41,42] following padding, the fabric was dried at 70 °C for 2 min using a Werner Mathis dryer.

2.6.3 Inkjet Printing

Inkjet printing was carried out on a Hewlett-Packard (HP) Deskjet 6940 thermal drop-on demand Colour Inkjet Printer with a single pass at a resolution of 1200 dpi. For each print trial, a solid rectangle print pattern was created using each of the inks formulated according to the procedure described elsewhere.[17] Prior to printing, each of the wool fabric samples was attached to a sheet of A4 transparency film using double sided tape for ease of passing through the paper-feeding system in the inkjet printer. The printed samples were allowed to air dry for 5 min.

2.6.4 Fixation and Washing off

The inkjet-printed, air-dried, samples were steamed at 102 °C for 5, 10, 15, 20 and 25 min respectively. The inkjet-printed wool fabrics were cold rinsed for 5 min, hot washed at 65 °C

(2 g.dm^{-3} Sandozin NIE and 5 g.dm^{-3} sodium bicarbonate) for 10 min and then rinsed in running tap water for 10 min.

2.7 Physicochemical Properties of the Inks

Surface tension of ink formulation was measured by Du Nouy method by using a Torsion balance (White Electrical Instruments Ltd, Malvern Link, UK) in which the force required to pull the ring from the liquid surface is measured.[43] Viscosity of ink formulations was measured using a Brookfield Viscometer DV-I Prime.

2.8 Stability of the Inks

In order to assess the stability of the dyes in ink formulations, each ink was allowed to stand at room temperature over a period of 6 months and the change in the content of the dissolved dye in the ink, as indicated by the integrated area of the elution peak in capillary electropherogram were recorded through CE (MEKC). Furthermore, for the ease of identification of dye peak in MEKC electropherogram, the stored ink sample was tested against fresh ink sample made on that particular day. Therefore, the capillary electropherograms presented are of samples tested for stability at the same time under the same CE conditions.

2.9 Colour Strength

Colour strength of the inkjet-printed wool fabrics was determined using the minimum reflectance method with a Datacolor spectrophotometer D650 using illuminant D65 and 10° standard observer. For reflectance measurement, each printed fabric was folded twice to give four layers of fabric to ensure opacity. The colour strength (K/S) values were calculated using the Kubelka–Munk Equation shown in Equation 1,

$$K/S = \frac{(1-R)^2}{2R} \qquad \text{Equation 1}$$

2.10 Dye Fixation

The percent dye fixation was determined using a Perkin Elmer Lambda 40 UV/Vis Spectrophotometer (UK) in order to calculate the dye concentration in the various wash-off solutions according to the procedure describe previously.[17,36,41]

2.11 Colour Fastness Properties

Light fastness and wash fastness test were carried out according to the BS EN ISO 105-B02 (Method 3)[44] and BS EN ISO 105-C06:2010 (A1S).[36,45]

3 RESULTS AND DISCUSSION

3.1 Synthesis of Reactive Dyes

Cyanuric chloride is an electron-poor heterocycle with its reactive chlorine atoms being easily substituted in nucleophilic aromatic substitution reactions. Furthermore, the reactivity of the remaining chlorine atoms depends upon the electrochemical character of the substitute and the positional relationship between the hetero-nitrogen atoms and substituent.[46,47]

The synthesis routes to prepare the reactive dyes used in this study are shown in Scheme 1. In the first step, the dichloro-s-triazine yellow dye **1a** was synthesised by coupling diazotised 7-amino-1,3-naphthalenedisulphonic acid with m-toluidine and then condensing with cyanuric chloride. The introduction of the first nucleophile (substituted amino **1**) to the cyanuric chloride afforded highly reactive dichloro-s-triazine dye **1a**. Then, 2-sulphophenoxy-4-chloro-s-triazine dye **1b** was synthesised by substituting only one of the labile chlorine atoms of dye **1a** with an ether linkage to 4-sulphophenyl group. Once the second substitution has taken place, the reactivity of the third chlorine atom differs from those of the first two. In this case, a phenoxy group is not as strong an electron donor as amino substituents so replacement of a chlorine atom with a phenoxy group will reduce reactivity of the remaining chlorine atom but to a lesser extent, producing a system of moderate reactivity.[46,48,49] Accordingly, 2-sulphophenoxy-4-chloro-s-triazine dye **1b** has a medium reactivity.

3.2 Capillary Electrophoresis (MEKC)

The micelles used in MEKC are charged on the surface, therefore an analyte having the opposite charge of the micelle will strongly interact with the micelle through electrostatic forces and an analyte having the same charge as the micelle will interact weakly, due to the electrostatic repulsion.[50] When anionic micelle such as sodium dodecyl sulphate (SDS) is employed, the general migration order will be: anions, neutral analytes and cations. Anions will remain mostly in the bulk solution due to electrostatic repulsions from the micelle; neutral molecules will be separated exclusively due to their hydrophobicity; while cations will migrate the slowest due to the strong electrostatic attraction.[51] As anionic analytes spend longer time in the bulk phase due to electrostatic repulsions from the SDS micelle; the greater the anionic charge, the more rapid the elution.[51] As SDS micelle was used in this study for the separation of yellow dyes **1a** and **1b**, they will interact weakly due to electrostatic repulsion, resulting in separation in the order of decreasing anionic charge.

Figure 1 shows the reaction progression of synthesis of dye **1a** in a fused silica capillary at pH 9.3. Both analytes have a charge of −2 under these conditions. As shown in Figure 1(b), water migrates quickly at the electroosmotic flow (EOF) velocity followed by yellow chromophore **1** (4.87 min) and then dye **1a** (5.49 min). This is because that dye **1a** has an increased molecular weight compared to yellow chromophore **1** but no additional sulphonate groups that would increase the solubility or hydrophilicity of the dye **1a.** Furthermore, the percent area of the the elution peak of dye **1a** shown in Figure 1(c) was 100% which indicates high purity of the final product.

Insert **Figure 1** here

Figure 2 shows the progression of the synthesis reaction from dichloro-triazine dye **1a** to the mono-substituted 2-sulphophenoxy-4-chloro-s-triazine dye **1b**. As shown in Figure 2(b), the dye **1b** migrates more quickly than the dye **1a**. This occurs because the mono substitution of dye **1a** with sulphophenoxy not only increases the molecular weight of dye **1b** but also increases a negative charge on it, therefore increasing the hydrophilicity of dye **1b**. In addition, MEKC analysis also shows that the starting material dye **1a** was fully converted to dye **1b** in 5 hours. Additionally, the percent area of the the elution peak of dye **1b** shown in Figure 2(c) was 100% which indicates high purity of the final product.

Insert **Figure 2** here

3.3 FT-IR Analysis

Analysis of FT-IR spectrum (Figure 3) of the pure dye powder obtained suggested that the compound is dye **1a** since peaks due to the presence of primary amine in yellow chromophore **1** (FT-IR spectrum not shown) at 1625 cm^{-1} no longer present indicating that the primary amine had successfully reacted with cyanuric chloride. According to literature,[38] triazine group has at least one strong band at 1580–1520 cm^{-1} and at least one band at 1450–1350 cm^{-1} corresponding to the stretching of the ring. The appearance of new peaks at 1542 cm^{-1} and 1386 cm^{-1} reflects the presence of the triazine group in dye **1a**. Moreover, in accordance with literature,[37,38] the appearance of the peaks at the 1097 cm^{-1} and 791 cm^{-1} are attributed to the stretching vibrations of carbon–chlorine bond on the triazine ring of the dye **1a**.

Insert **Figure 3** here

In FT-IR spectrum of dye **1b** (Figure 4), the new peak at 1120 cm^{-1} is evident which can be attributed to the stretching vibration of C–O–C in its structure between the triazine and the sulpho-phenoxy. The peak at 797 cm^{-1} can be attributed to the presence of C−Cl after the mono-substitution of dye **1a** by sulphophenoxy group.

Insert **Figure 4** here

3.4 Physicochemical Properties of the Inks

Surface tension and viscosity of the dyes **1a** and **1b** based inks are shown in Table 1. The data in Table 1 indicates that both inks exhibited surface tension and viscosity within the operational range of 25 – 60 $dynes.cm^{-1}$ and 2 – 20 cP, respectively.[1,30]

Insert **Table 1** here

3.5 Stability of the Inks

The percent area of peaks on the MEKC electropherogram is related to the concentration of specific compounds within the samples. The results of any change in percent area of the peaks of the **1a** and **1b** dyes based inks stored at room temperature for six months can be seen in Figures 5 and 6.

As can be seen from Figures 5(a–b) and 6(a–b), the percent area of dye **1a** decreases from 100% to 5% after only fifteen days of storage, whereas, for dye **1b** the percent area does not show any significant decrease during storage for six months. These results clearly reflect the difference in reactivity between the dyes. The instability of dye **1a** based ink is most likely due to the hydrolysis of one or both of the chlorine atoms under storage conditions. Such results are in-line with data presented by Glover [52] who found that reactive dyes of the highest reactivity possess the lowest stability. In addition, the high stability of dye **1b** based ink could be due to its medium reactivity, thus, less susceptibility towards hydrolysis, therefore increasing the overall stability of ink.

Insert **Figure 5** here

Insert **Figure 6** here

3.6 Printing Properties

As discussed previously, the chlorine atoms of cyanuric chloride are rapidly substituted by nucleophiles. This phenomenon is exploited in textile dyeing and printing. Triazine reactive group serves as an anchor and links the dye covalently to the wool fibre making the dyed/printed fibre colourfast. The synthesised dyes **1a** and **1b** are capable of reacting with amino (–NH_2), thiol (–SH) and hydroxyl (–OH) groups of wool fibre through nucleophilic aromatic substitution reaction. Figure 7 presents the digital photos of the inkjet-printed wool fabrics.

Insert **Figure 7** here

3.6.1 Steaming Conditions

Figure 8 shows the effect of steaming time on colour strength and dye fixation of dichloro-s-triazine (**1a**) and 2-sulphphenoxy-4-chloro-s-triazine (**1b**) dyes onto inkjet-printed wool fabric. From Figures 8(a–b), it is evident that increasing the steaming time from 5 to 25 min at 102 °C, brings about an increase in colour strength and dye fixation of inkjet-printed dyes, reflecting the positive impact of steaming on printing properties. It is generally agreed that during steaming process, steam condenses on the fabric. The thickening agent and fiber therefore swells and the dyestuff diffuses into the fiber polymer system. The high temperature promotes solution and accelerates the rate of diffusion of the dyestuff resulting in increased extent of formation of covalent bonds.[53,54]

It can also be seen from Figure 8(a–b) that the 2-sulphophenoxy-4-chloro-s-triazine dye **1b** exhibited superior printing properties to those achieved by dichloro-s-triazine dye **1a**. These results clearly reflect the difference in the reactivity of both dyes. The comparatively lower reactivity exhibited by the 2-sulphophenoxy-4-chloro-s-triazine dye **1b** makes it ideally suited for inkjet printing process, whereas, the dichloro-s-triazine dye **1a**, being highly reactive, not only reacts with wool but also hydrolyses under selected conditions of fixation and results in moderate fixation.[55]

It is also evident from Figure 8(a–b) that 10 min is an ideal time for fixation of dye **1a** onto wool owing to its high reactivity, whereas, 20 min is required for the new dye **1b** owing to its lower reactivity which necessitates longer steaming time in order to achieve higher dye fixation.

Insert **Figure 8** here

3.7 Wash Fastness

Wash fastness properties of the wool fabric inkjet-printed with the synthesised yellow dyes **1a** and **1b** are shown in Table 2. It was found that Yellow dye **1a** showed good to excellent wash fastness resulting in a grade 4–5; and slight to negligible staining on adjacent cotton fabric whereas dye **1b** showed excellent wash fastness properties and no staining on adjacent multi fibres. This excellent wash fastness of dye **1b** may be attributed to the covalent bonding between the dye and the wool fibre.[56]

3.8 Light Fastness

Table 2 shows the light fastness properties of the wool fabric inkjet-printed with the synthesised yellow dyes **1a** and **1b**. Both dyes **1a** and **1b** passed target wool reference 6 and 6^+, respectively. However, the light fastness of **1b** was 0.5 grade greater than **1a**. Such a result may be attributed to the formation of covalent bond between dyestuff and fibre which seems to facilitate the transfer of energy from excited state of the dye molecule to fiber resulting in increased stability of the reacted dyes.[56]

Insert **Table 2** here

4 CONCLUSIONS

A dichloro-s-triazine dye was synthesised and converted to a new medium reactivity reactive dye containing 2-sulphophenoxy-4-chloro-s-triazine. The physicochemical properties, such as surface tension and viscosity of formulated inks, were found to be in the operational range. The newly synthesised 2-sulphophenoxy-4-chloro-s-triazine dye showed excellent stability towards hydrolysis over six months' time making the dye ideally suited for inkjet printing. Also, the 2-sulphophenoxy-4-chloro-s-triazine dye showed a significantly higher colour strength and dye fixation when compared with the dichloro-s-triazine dye due to its medium reactivity. With respect to the light fastness properties, the 2-sulphophenoxy-4-chloro-s-triazine dye gave 0.5 grade higher light fastness than dichloro-s-triazine dye. Moreover, the 2-sulphophenoxy-4-chloro-s-triazine showed excellent wash fastness properties. As a result, it is believed that the new reactive dye based ink has paved the way for a more sustainable inkjet printing of wool fabrics thanks to having prolonged shelf-life and substantially improved dye fixation.

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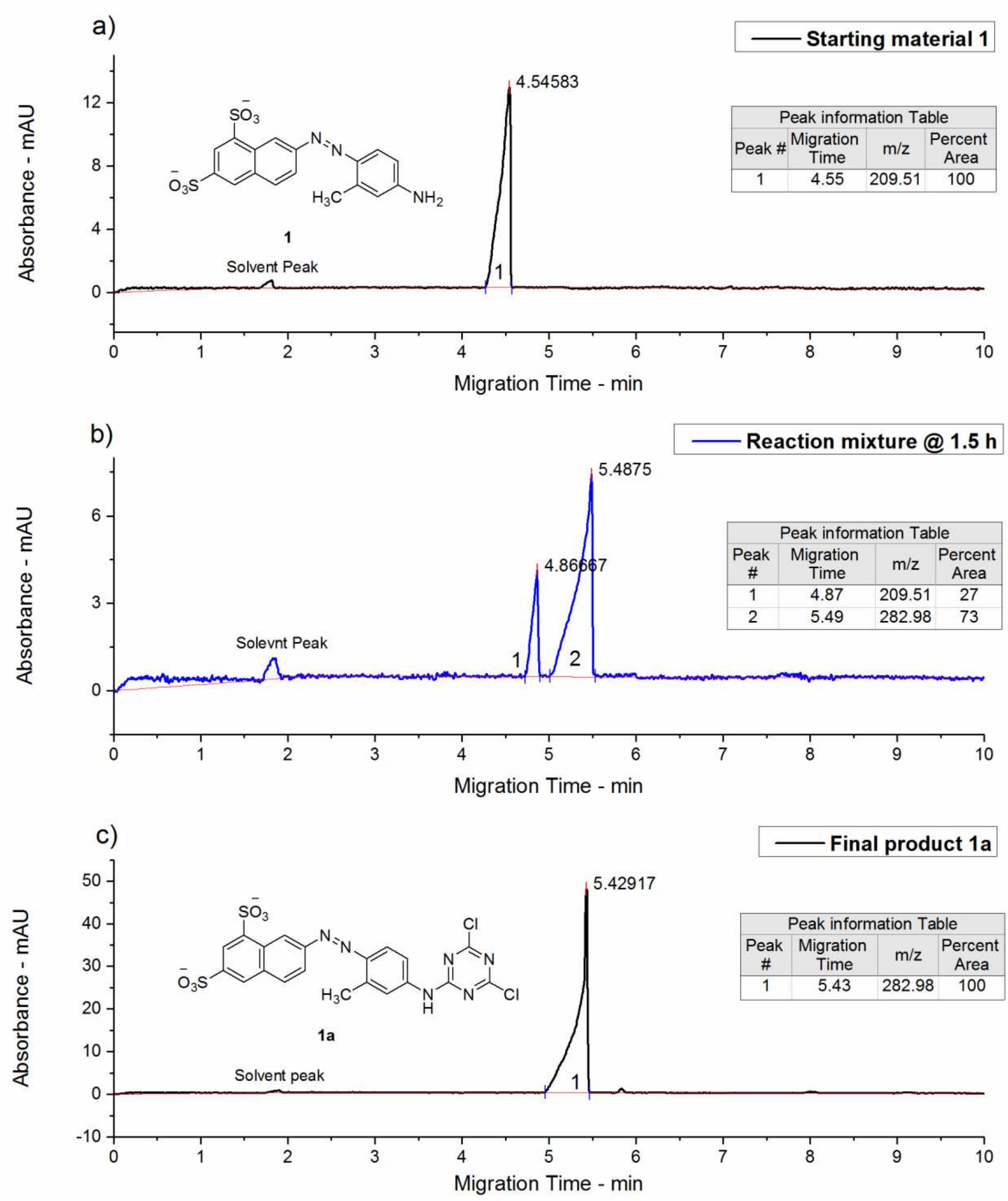


Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	4.55	209.51	100

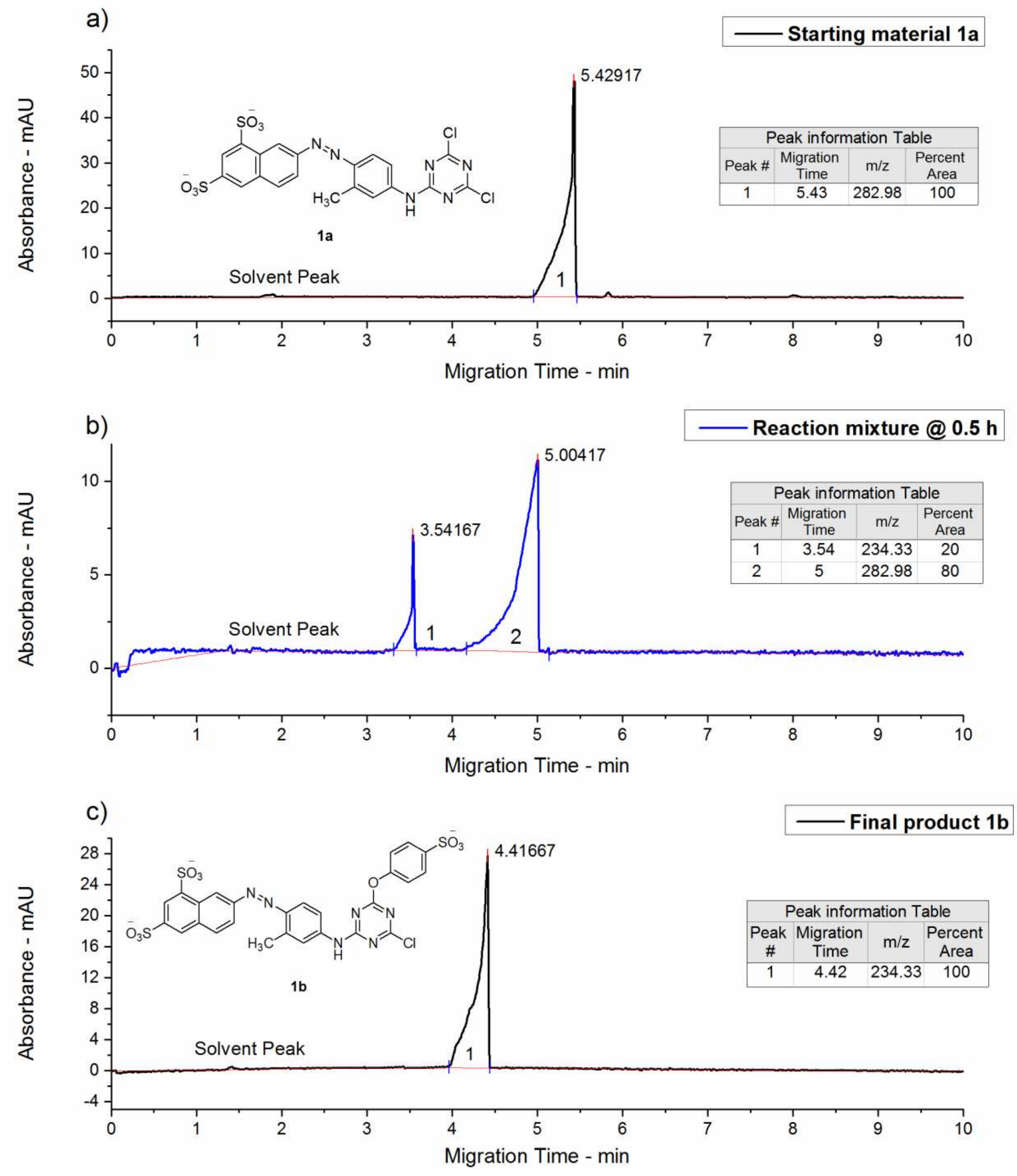
Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	4.87	209.51	27
2	5.49	282.98	73

Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	5.43	282.98	100

Figure 1



Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	5.43	282.98	100

Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	3.54	234.33	20
2	5	282.98	80

Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	4.42	234.33	100

Figure 2

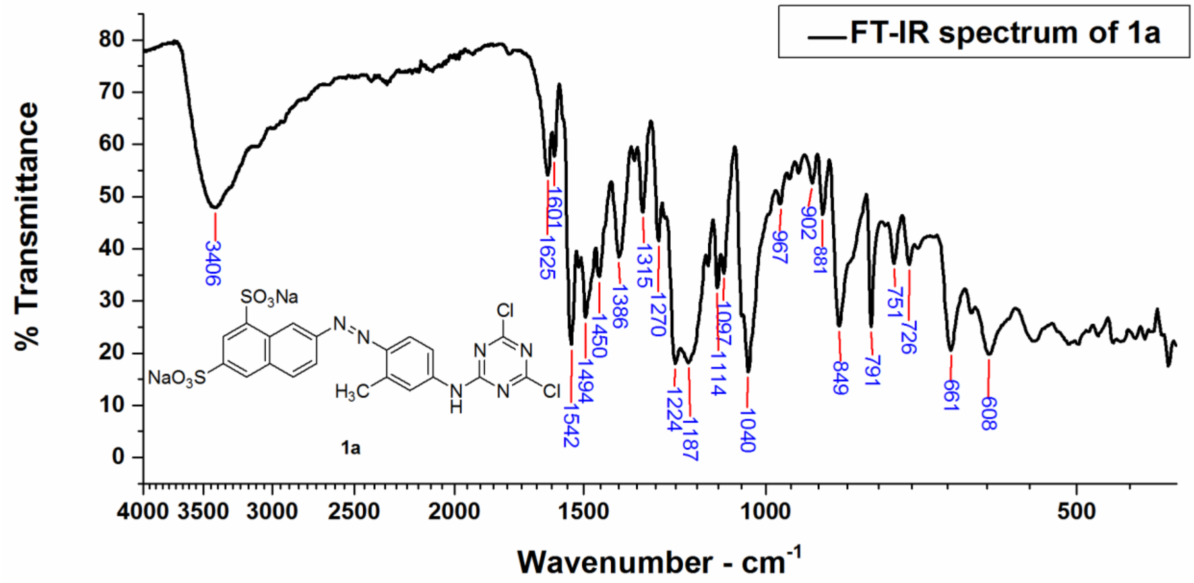

FT-IR spectrum of 1a
% Transmittance
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber - cm^{-1}
3406
1601
1625
1542
1494
1450
1386
1315
1270
1224
1187
1114
1097
1040
967
902
881
849
791
751
726
661
608
SO$_3$Na
NaO$_3$S
N
N
Cl
N
N
N
Cl
H$_3$C
N
H
1a

Figure 3

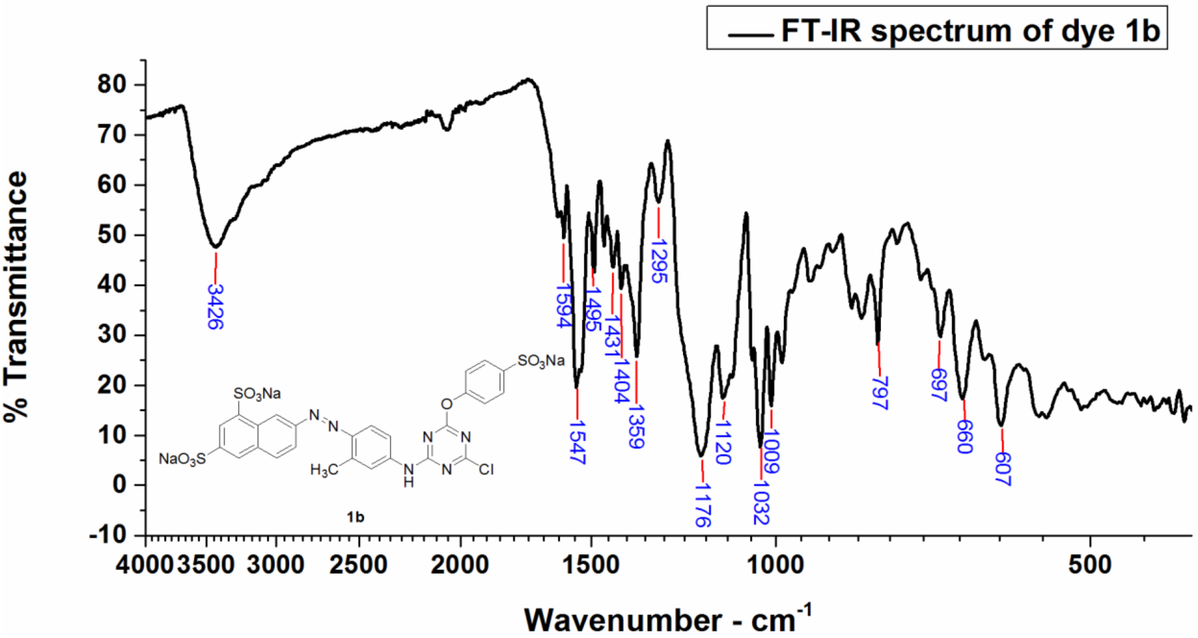
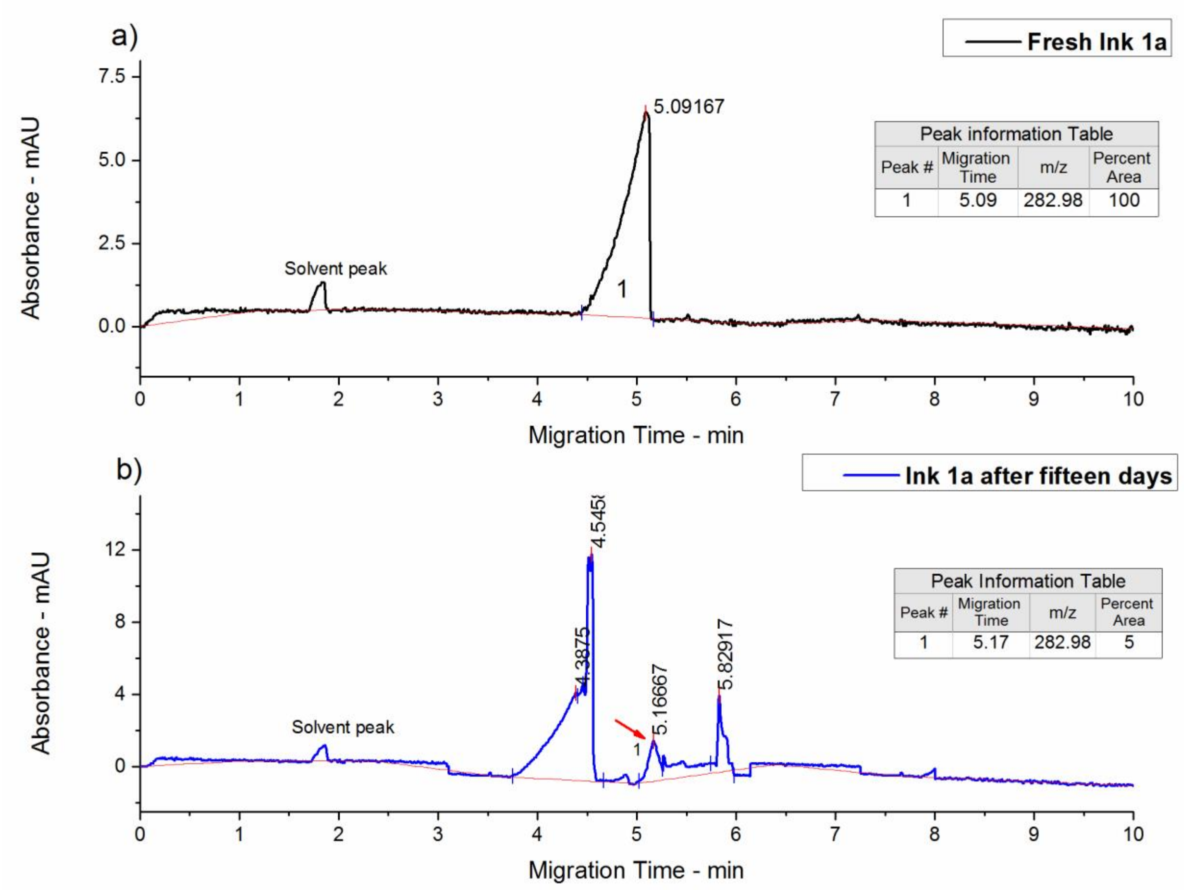

FT-IR spectrum of dye 1b
% Transmittance
Wavenumber - cm-1
80
70
60
50
40
30
20
10
0
-10
4000
3500
3000
2500
2000
1500
1000
500
3426
1594
1495
1431
1404
1359
1295
1547
1176
1120
1032
1009
797
697
660
607
SO3Na
NaO3S
SO3Na
N
N
H3C
N
H
O
N
N
N
Cl
1b

Figure 4



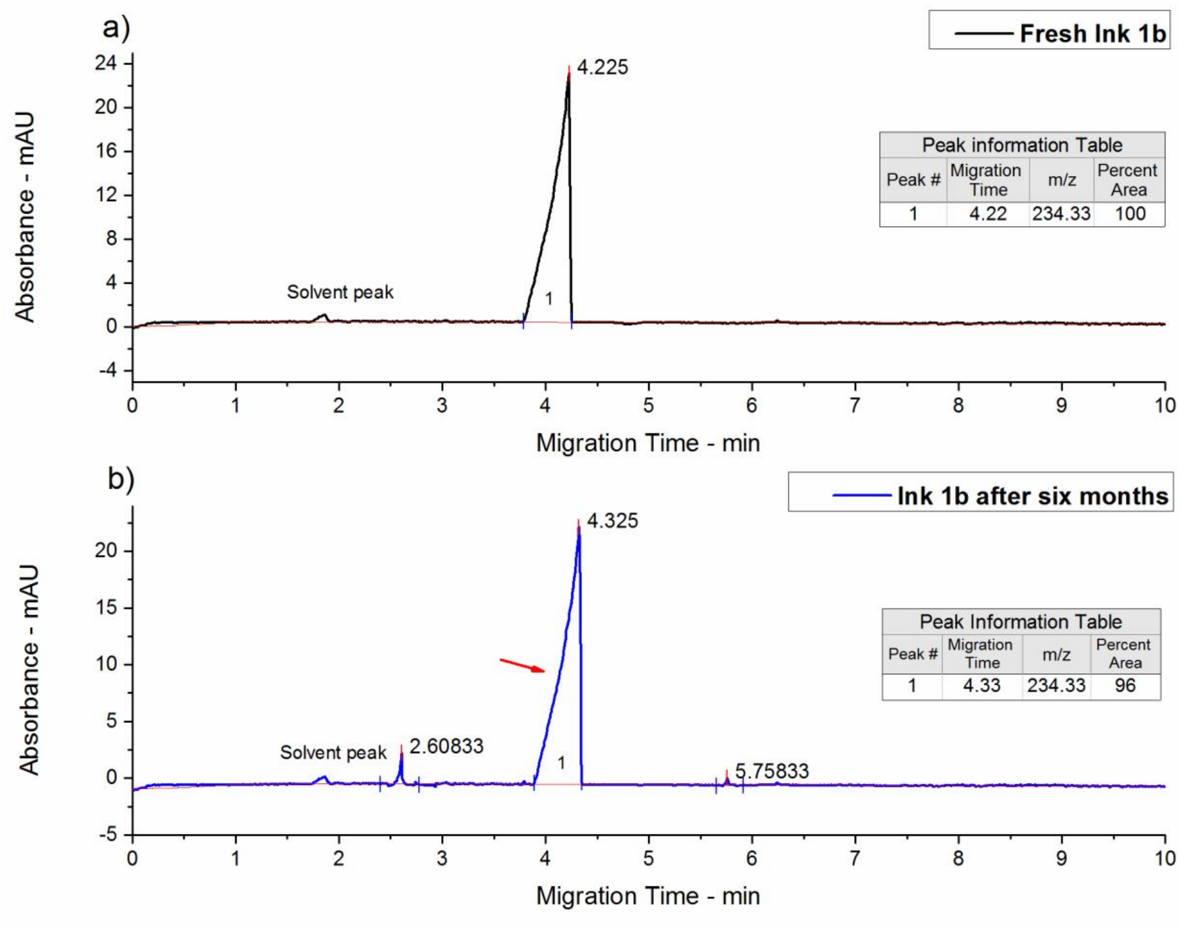
Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	5.09	282.98	100

Peak Information Table

Peak #	Migration Time	m/z	Percent Area
1	5.17	282.98	5

Figure 5



Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	4.22	234.33	100

Peak Information Table

Peak #	Migration Time	m/z	Percent Area
1	4.33	234.33	96

Figure 6

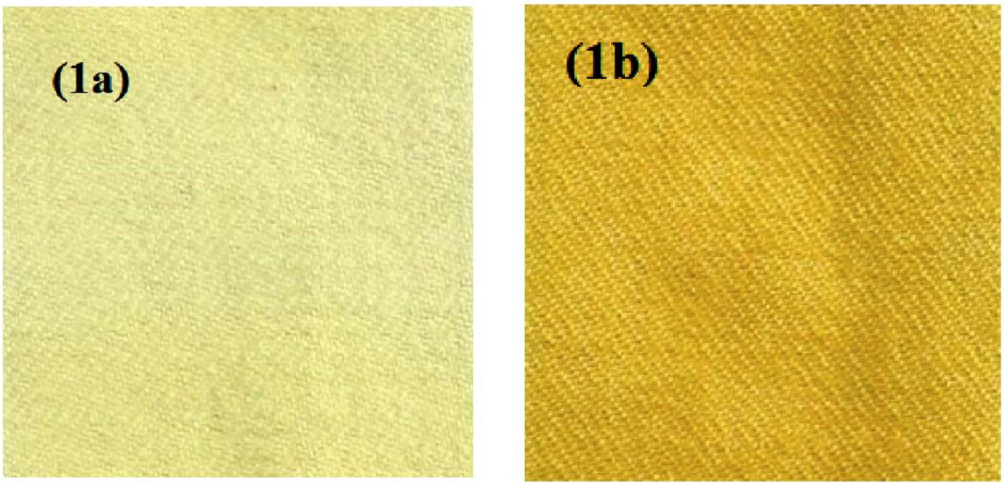


Figure 7

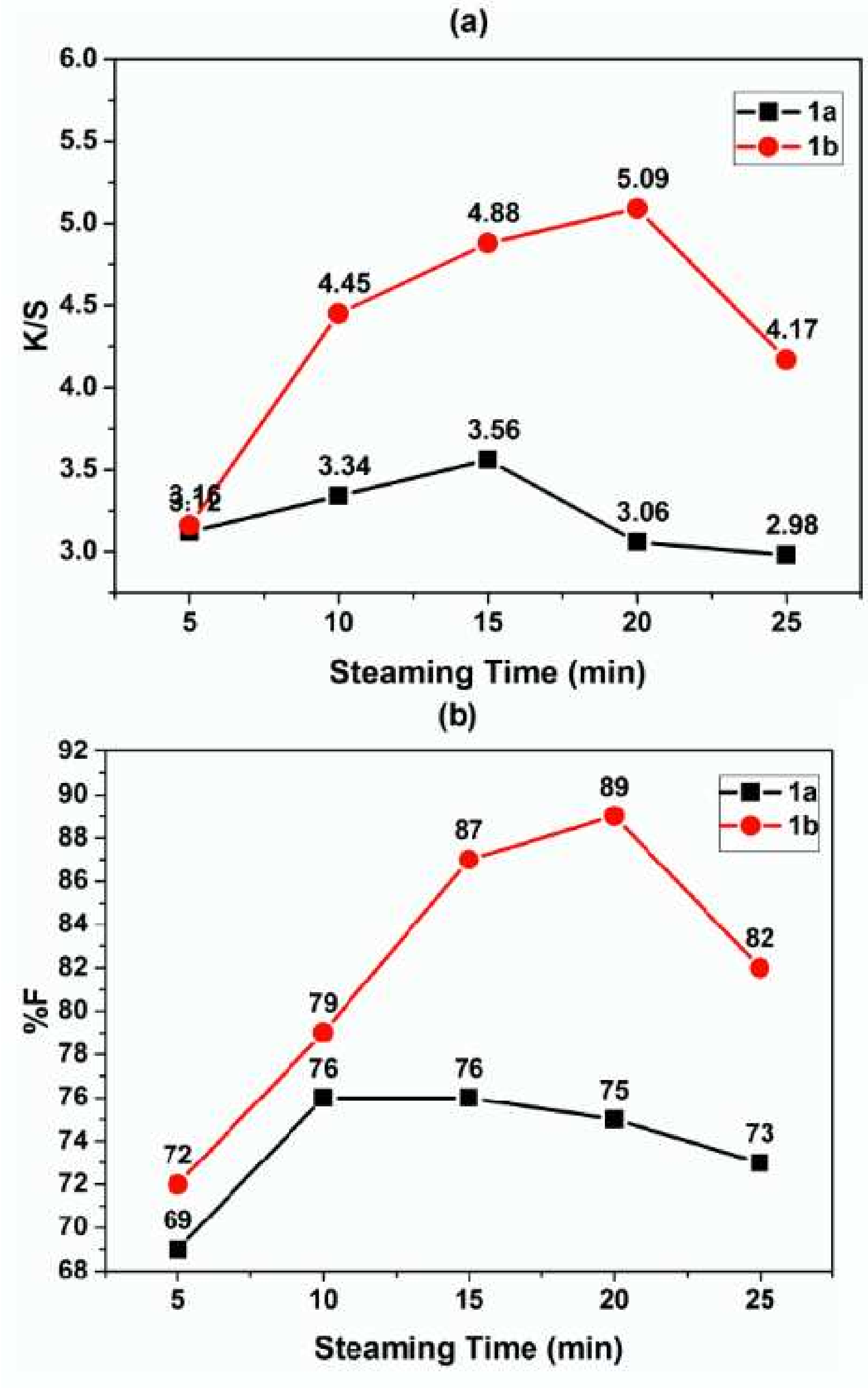

(a)
K/S
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Steaming Time (min)
5
10
15
20
25
1a
1b
3.16
3.12
4.45
4.88
5.09
4.17
3.34
3.56
3.06
2.98
(b)
%F
92
90
88
86
84
82
80
78
76
74
72
70
68
Steaming Time (min)
5
10
15
20
25
1a
1b
72
79
87
89
82
69
76
76
75
73

Figure 8

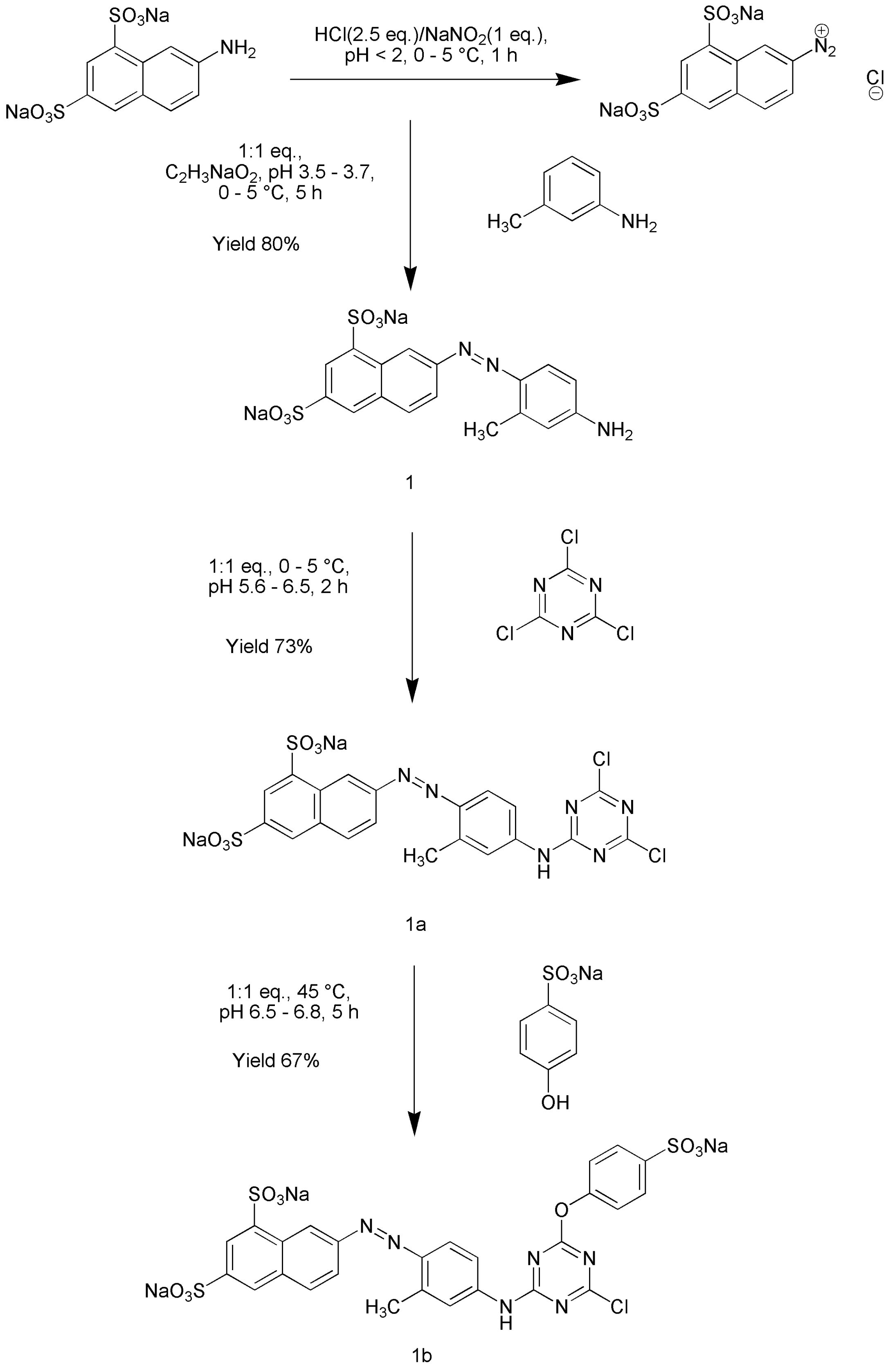
TABLE 1 Surface Tension and Viscosity of the Yellow Inks

Ink	**Surface Tension** (**dynes.cm^{-1}**)	**Viscosity** (**cP**)
Dye 1a	44.5	8
Dye 1b	44.5	6

TABLE 2 Fastness Properties of Yellow Dyes on Wool Fabric

Dye/Ink	**Change in shade**	**Staining**						**Light Fastness**
		CA	**C**	**N**	**P**	**A**	**W**	
Dye 1a	4-5	5	4-5	5	5	5	5	6
Dye 1b	5	5	5	5	5	5	5	6+

CA: Cellulose Acetate; C: Cotton; N: Nylon; P: Polyester; A: Acrylic; W: Wool


HCl(2.5 eq.)/NaNO2(1 eq.),
pH < 2, 0 - 5 °C, 1 h
1:1 eq.,
C2H3NaO2, pH 3.5 - 3.7,
0 - 5 °C, 5 h
Yield 80%
1
1:1 eq., 0 - 5 °C,
pH 5.6 - 6.5, 2 h
Yield 73%
1a
1:1 eq., 45 °C,
pH 6.5 - 6.8, 5 h
Yield 67%
1b

Scheme 1