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Green Synthesis of Reactive Dye for Inkjet Printing

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Abstract

Chloropyrimidine based reactive dyes are reported to be well suited for textile printing; however, nucleophilic aromatic substitution of chloropyrimidines with amino-containing chromophores is slow and often suffers poor yields. In this study, a novel and simple method has been developed for the synthesis of chloropyrimidine based reactive dye under microwave irradiation. In addition, the dye was also synthesised by conventional heating for comparison. Such a comparison took the reaction time and yield into account. The progress of the syntheses reactions concerned was monitored using Capillary Electrophoresis (CE) and the purity of the dye obtained was assessed by thin layer chromatography (TLC). The synthesised trichloropyrimidine dye was confirmed by Fourier-transform infrared spectrometry and elemental analysis. It was found that the reaction rate of the nucleophilic aromatic substitution carried out under microwave irradiation was four times greater than that carried out under conventional heating, although the enhancement in product yield was modest. These results suggest that microwave irradiation is an effective technique for the synthesis of chloropyrimidine based reactive dyes. The synthesised chloropyrimidine dye was formulated into an ink and applied onto a wool fabric by inkjet printing. The printed fabrics were steamed at 102 °C for 5–25 min at 5 min intervals. Good colour strength and rate of dye fixation were obtained, both of which increased with increasing steaming time. The prints obtained exhibited reasonably good light and wash fastness properties.

Key Terms

Microwave irradiated synthesis; Reactive dyes; Chloropyrimidines; Inkjet printing; Wool

1 INTRODUCTION

Inkjet printing possesses a number of advantages such as mass customisation, unlimited design possibilities with respect to colour range and repeat size, elimination of the set-up cost associated with screen preparation and cost effective short run production, over traditional screen printing.[1,2] However, inkjet printing also has its disadvantages including its relatively lower productivity and limitations in available dye selection for inks. To obtain good printing properties, the dyes for inkjet printing inks have to satisfy certain criteria such as excellent storage stability, low to medium reactivity and high solubility.[2,3,4,5]

Pyrimidine based reactive dyes especially trichloropyrimidine dyes are an important and slightly less reactive class of reactive dyes.[6] It is well established that trichloropyrimidine based reactive dyes are well suited for textile printing due to their low reactivity, high stability, high solubility and ease of removal of unfixed dye.[6,7] These properties make trichloropyrimidine based reactive dyes an ideal candidate for use in inkjet printing inks for textiles.[8] However, it is also well documented that the nucleophilic aromatic substitution of chloropyrimidines with amino-containing chromophore is slow and generally requires vigorous reaction conditions such as high temperatures and long reaction times and also suffers poor yield.[6,9] Thus, despite several advantages, the potential of chloropyrimidine based reactive dyes for use in inkjet printing inks have not been fully explored.

In recent years, microwave irradiated synthesis has emerged as an efficient tool in modern organic synthesis chemistry.[10,11,12,13] Microwave irradiation has several advantages over conventional heating for organic syntheses, such as reduced reaction times, enhanced yields and less negative impacts on environment.[14] It is believed that in the case of microwave irradiation, the electromagnetic field that interacts with molecules via dipole rotation and ionic conduction is primarily responsible for generation of heat.[13] In the dipolar rotation, a molecule rotates back and forth constantly, attempting to align its dipole with the ever-oscillating electromagnetic field; the friction between each rotating molecule results in heat generation. In the ionic conduction, a free ion or ionic species moves translationally through space, attempting to align with the changing electromagnetic field. Like in the dipolar rotation, the friction between these moving species results in heat generation.[15] In both cases, the more polar and/or ionic the reactant and solvent, the more efficient the rate of heat generation resulting in a significant increase of reaction rates often accompanied by an increased yield.[14] Despite several advantages, the use of microwave irradiation for dye synthesis has so far been limited to cyanine dyes[16,17,18,19] and more recently to disperse dyes.[20,21] To the best of the authors' knowledge, there has been no published report on the synthesis of reactive dyes under microwave irradiation.

Herein, we report the authors' successful attempt in preparation of trichloropyrimidine reactive dye, a promising class of reactive dyes for reactive inks, under microwave irradiation. Relevant results obtained and observations made from such microwave irradiation syntheses were compared and contrasted with those that pertain to syntheses using conventional heating. Inkjet printable inks containing the dyes synthesised were prepared, characterised, and inkjet-printed onto wool fabrics and steamed for various lengths of time. The fastness properties of the printed fabrics were also evaluated.

2 EXPERIMENTAL

2.1 Materials

7-amino-1,3-naphthalenedisulphonic acid (88%), sodium nitrite (98%), m-toluidine (99%), tetrachloropyrimidine (99%), sodium phosphate dibasic (>99%), sodium phosphate monobasic (99%) and acetone (ACS reagent, ≥99.5%) were purchased from Sigma-Aldrich 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 throughout this work.

The digital printing auxiliaries for wool fabric pretreatment included Sodium metabisulphite (Sigma-Aldrich), carboxymethyl cellulose (Sigma-Aldrich), urea (MP Biomedicals), and alcopol O 60 (Acros Organics). Material used for the formulations of inks included N-methylmorpholine N-oxide (Sigma-Aldrich), polysorbate 20 (Sigma-Aldrich), 2-pyrrolidone (Acros Organics), and propan-2-ol (Fisher). Sandozin NIE (Clariant) was used in washing-off.

2.2 Methods and Instrumentation

A Discover SP microwave (CEM Corporation) interfaced to a personal computer running the Synergy software was used to generate microwave irradiation. This system featured a single-mode microwave cavity that was capable of accommodating a 10 cm^3 or a 35 cm^3 sealed reaction vessels, and of sustaining pressures up to 30 bars. The Discover SP microwave was incorporated with both pressure and temperature feedback systems for the monitoring and controlling of the reaction conditions. An infrared temperature sensor was used to measure the temperature of the reaction mixture.

Micellar Electrokinetic Chromatography (MEKC) analyses were carried out on a Beckman P/ACE MDQ interfaced with P/ACE station software. A capillary tube having a 50 μm internal diameter, a length to the detector of 30 cm and a total length of 40.2 cm was used. Throughout the analysis, the capillary tube was cooled to 30 °C. The samples to be analysed were prepared in deionised water and injected at a pressure of 0.5 psi over a period of 10 s. A fixed voltage of 25 kV was applied over the capillary tube to enhance the separation of peaks. The analytes detector was set at 420 nm. The elution buffer used contained 20 mM sodium tetraborate and 50 mM sodium dodecyl sulphate in deionised water (pH 9.3). New buffers were used after every ten runs to minimise the potential occurrence of irreproducible electroosmotic flow and migration times that might result from evaporation of solvent in the buffers.[22] The raw data generated by the MEKC were analysed and peaks were integrated using OriginPro 9.0.0.

Thin layer chromatography (TLC) was performed using iso-butanol–n-propanol–ethyl acetate–water as eluent[16,17] and aluminium plates coated with silica gel 60 F_{254} (Merck) as stationary phase. The developed plates were visualised in visible light as well as under both short and long wavelength ultraviolet light (254 nm, 365 nm) and retention factor (R_f) were calculated.

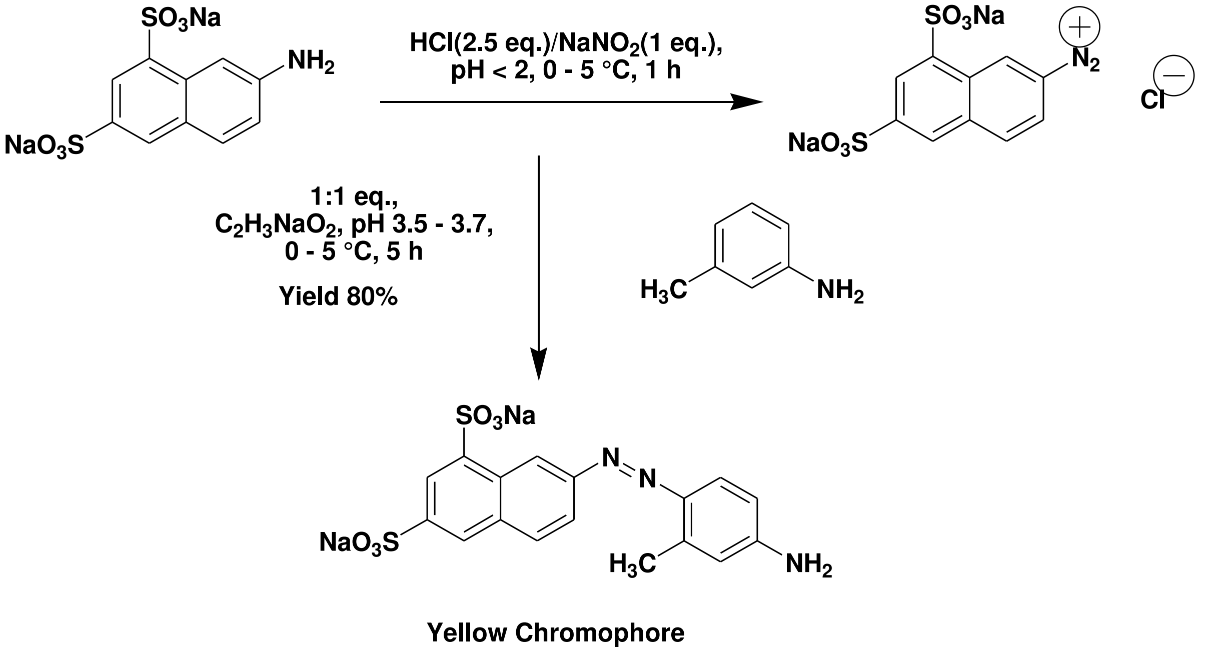
Infrared spectra were recorded using a Spectrum One spectrophotometer (Perkin Elmer, UK) equipped with a Perkin Elmer Diamond Golden Gate sampling attachment for attenuated total reflection (ATR) measurements. Each spectrum was acquired at a 4 cm^{-1} resolution, a scan speed of 0.5 cm/s and 100 scans per spectrum. The operating software used was the Perkin Elmer Spectrum 5.0.1. The raw data obtained were analysed using OriginPro 9.0.0. The vibrational frequencies are reported in wavenumbers (cm^{-1}).

Elemental analyses for carbon, hydrogen and nitrogen were performed using a FlashEA 1112 analyser supplied by Thermo Scientific.

2.3 Synthesis of Yellow 7-[(4-amino-2- methylphenyl)azo]-1,3-naphthalenedisulphonic-acid dye (chromophore)

In the study reported here, a yellow chromophore was synthesised in accordance with the procedure described in earlier studies.[23,24,25,26] 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 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 completed 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 by adding sulphamic acid.

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 at 0 to 5 °C over 45 minutes. The pH of the reaction mixture was then adjusted to 3.5 to 3.7 by the addition of 2N sodium acetate solution and the reaction mixture was stirred for further 4 hours at 0 to 5 °C. Solid sodium chloride to give 8% *w/v* final concentration was added in small portions to the 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 dye chromophore using solvent-nonsolvent technique (dimethylformamide-acetone, 1:2 *v/v*)[27,28,29] yielded pure reddish yellow powder (18.62 g, 40.0 mmol, yield 80%). The reaction is shown in Scheme 1.



SCHEME 1 Diazotization of 7-amino-1,3-naphthalenedisulphonic acid and coupling of diazonium salt with m-toluidine to yield yellow dye chromophore

Analytics: Yellow dye chromophore structure was confirmed by FT-IR;[30,31,32,33] 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 cm^{-1}; 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}.

The assignments of ^1H NMR (D_2O, 500 MHz) shifts are as follows: δ 2.30 (3H, s), 6.38 (1H, s), 6.41 (1H, J = 10 Hz, d), 7.30 (1H, J = 10 Hz, d), 7.77 (1H, J = 10Hz, d), 7.91 (1H, J = 10, d), 8.22 (1H, s), 8.29 (1H, s), 8.68 (1H, s).

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.

MEKC Migration Time (4.55 min); R_f (0.63); Purity (100%).

2.4 Synthesis of Yellow 7-[(2,5,6-trichloro-4-pyrimidinyl)amino]-2-[(methylphenyl)azo]-1,3-naphthalenedisulphonic-acid dye (1)

2.4.1 Synthesis Aided by Microwave Irradiation

Yellow dye chromophore (0.465 g, 1 mmol, 1 eq.) and 2,4,5,6-tetrachloropyrimidine (0.238 g, 1.1 mmol, 1.1 eq.) were added to each of ten 35 cm^3 borosilicate reaction vessels followed by addition of 10 cm^3 of sodium phosphate buffer [Na_2HPO_4 (0.20 M, 2 cm^3) and NaH_2PO_4 (0.12 M, 8 cm^3), pH 7.0] and 10 cm^3 of acetone. The vessels were then capped and placed in the reaction cavity of the microwave device. The temperature was ramped from room temperature to 55 °C, and the reaction was allowed at this temperature for 90 min with stirring. After cooling at room temperature, the resulting reaction mixtures were combined and solid sodium chloride to give 8% *w/v* final concentration was added to precipitate the dye. The crude dye was isolated via vacuum filtration; washed with 200 cm^3 of sodium chloride solution (10% *w/v*) and dried *in vacuo* (40 °C, 12 hours). Purification of the crude dye using solvent-nonsolvent technique (dimethylformamide-acetone, 1:2 *v/v*)[27,28,29] afforded the pure dye **1** (5.41 g, 8.36 mmol, yield 84%) as yellow powder.

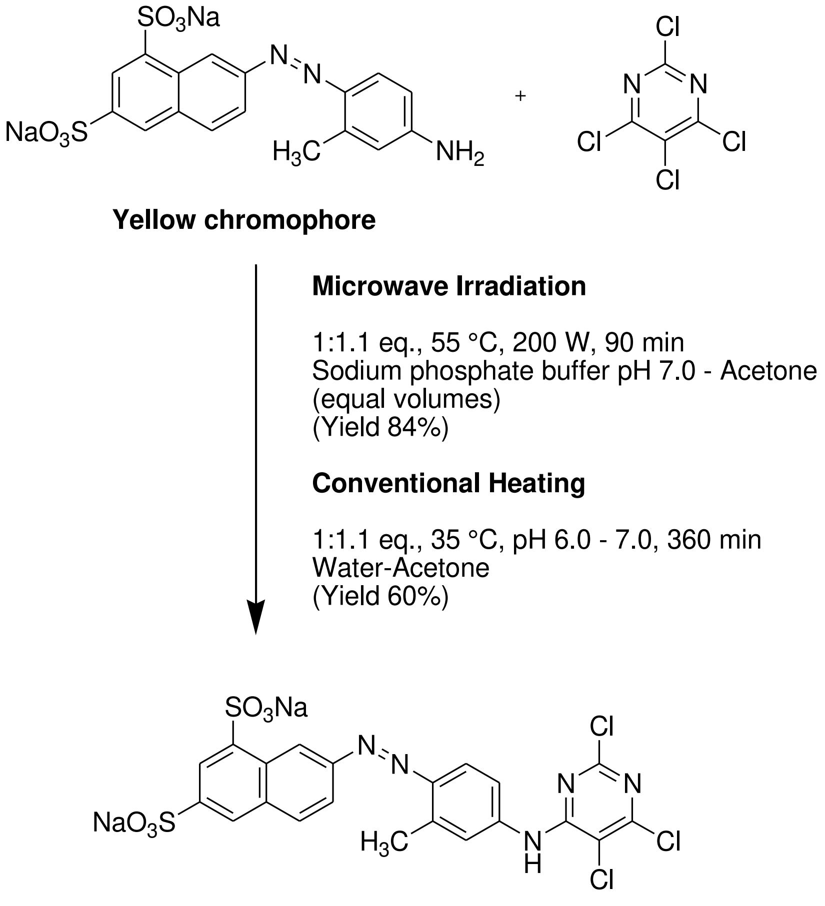
Analytics: Yellow dye **1** structure (prepared by Microwave irradiation method) was confirmed by FT-IR;[30,31,32,33] N-H stretch, 3401 cm^{-1}; overtone or combinational bands, 2000–1667 cm^{-1}; N-H bend, 1597 cm^{-1}; C=C ring stretch, 1567 cm^{-1}, 1496 cm^{-1}; azo group stretch, 1448 cm^{-1}; C=N stretch, 1538 cm^{-1}, 1387 cm^{-1}; C-N stretch, 1336 cm^{-1}; sulphonate, 1193 cm^{-1}; C-Cl stretch, 1098 cm^{-1}, 849 cm^{-1}; in-plane C-H bend, 1048 cm^{-1}, 1011 cm^{-1}; out of plane aromatic C-H bend, 754 cm^{-1}; CH_3 rock 726 cm^{-1}.

Elemental analysis, found: C, 38.98%; H, 1.87%; N, 10.81%, calculated for $C_{21}H_{12}Cl_3N_5Na_2O_6S_2$: C, 38.99%; H, 1.87%; N, 10.83%.

MEKC Migration Time (6.94 min); R_f (0.66); Purity (100%).

2.4.2 Synthesis Aided by Conventional Heating

Yellow dye chromophore (4.65 g, 10 mmol) was dissolved in water (50 cm^3) which was adjusted to pH 7.0 by the addition of 2N sodium carbonate solution at 35 °C. A solution of tetrachloropyrimidine (2.38 g, 11 mmol) in acetone (50 cm^3) was added as thin stream for a period of 10 min to the dye chromophore solution. Once the addition of 2,4,5,6-tetrachloropyrimidine was complete, the reaction mixture was stirred and the pH was maintained at 6.0 – 7.0 by the addition of 2N sodium carbonate solution. The reaction was stirred for 6 hours (until the pH had stabilised) at 35 °C. After adjusting pH of the reaction mixture to 7.0 using sodium carbonate solution (2N), solid sodium chloride to give 8% *w/v* final concentration was added to precipitate the dye. The reaction mixture was filtered and the crude dye was collected and was washed with a 200 cm^3 of sodium chloride solution (10% *w/v*) and dried in *vacuo* (40 °C, 12 hours). The crude dye was purified via the same process as mentioned in microwave irradiation method and afforded pure dye **1** (3.86 g, 5.96 mmol, yield 60%) as yellow powder. The reaction is shown in Scheme 2.



1

SCHEME 2 Nucleophilic aromatic substitution of 2,4,5,6-tetrachloropyrimidine with yellow dye chromophore to yield yellow dye **1** under microwave irradiation and conventional heating

2.5 Inkjet Printing Procedure

2.5.1 Ink Preparation

The ink was formulated using following composition in deionised water: synthesised yellow dye **1** (40 g.dm^{-3}; prepared by microwave irradiation method), 2-pyrrolidone (20 g.dm^{-3}), N-methylmorpholine N-oxide (300 g.dm^{-3}), propan-2-ol (25 g.dm^{-3}) and polysorbate

20 (10 g.dm^{-3}). The formulated ink was placed inside an ultrasonic-water bath for 10 min and then filtered using a 1 μm filter prior to use.[22]

2.5.2 Fabric Pretreatment

The wool fabrics were padded with 100% wet pick-up using pretreatment liquor of following composition: carboxymethyl cellulose (20 g.dm^{-3}), sodium metabisulphite (20 g.dm^{-3}), urea (300 g.dm^{-3}), and Alcopol O 60 (5 g.dm^{-3}).[34,35,36] After padding, the fabric samples were dried at 70 °C for 2 min using a Werner Mathis dryer.

2.5.3 Inkjet Printing of Ink onto Wool Fabrics

Inkjet printing of the formulated ink was carried out on a commercially available office inkjet printer, Hewlett-Packard Deskjet 6940 thermal drop-on-demand inkjet printer. A solid rectangle pattern was printed using the formulated ink with single pass at a resolution setting of 600 dpi. For the purpose of feeding them through the inkjet printer without distortion, each of the fabric samples was attached to a sheet of A4 size transparency by applying double sided tape to the fabric edges. Printed samples were allowed to dry in air for 5 min at ambient temperature and then steamed at 102 °C for 5 – 25 min at 5 min intervals. After steaming, the inkjet-printed wool fabrics were rinsed with cold water for 5 min in 100 cm^3 water, soaped with 100 cm^3 solution containing 2 g dm^{-3} Sandozin NIE and 5 g dm^{-3} sodium bicarbonate at 95 °C for 10 min, and then finally rinsed with 100 cm^3 cold water for 10 min. The rinsed samples were then dried under standard laboratory conditions of 20 ± 2 °C and 65 ± 2% relative humidity (RH).

2.6 Measurement of Colour Strength

Colour strength of the inkjet-printed wool fabrics was determined using Datacolor spectrophotometer D650 using illuminant D65 and 10° standard observer. For colour strength measurements, the printed fabrics were folded twice. The colour strength (K/S) values were calculated using the Kubelka–Munk Equation shown in Equation (1),

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

2.7 Measurement of Dye Fixation (%F)

For the assessment of dye fixation (%F), the method adopted was based on UV/Vis spectrophotometric measurements[37,38,39,40] of the liquor collected during washing of the unfixed print and during washing of the prints that were subjected to different steaming times. For this purpose, Perkin Elmer Lambda 40 UV/Vis spectrophotometer was used and the detailed procedure is as follows. The printed sample that was not subjected to steaming was immediately rinsed for 5 minutes in 100 cm^3 cold water. This was followed by soaping in 100 cm^3 aqueous solution of 2 $g.dm^{-3}$ of Sandozin NIE and 5 $g.dm^{-3}$ of sodium bicarbonate at 95 °C for 10 min. Subsequently, the sample was rinsed again for 10 min in 100 cm^3 cold water. For spectroscopy, these wash-off solutions were collected and an aliquot of 75 cm^3 was extracted and diluted to 100 cm^3 with distilled water. The absorbance of this liquor which was referred to as A_o, was measured at the wavelength of maximum absorption (λ_{max}= 420 nm). In exactly the same manner, the rinse liquors for the printed samples that were subjected to various steaming times were collected and their absorbance was referred to as A_i. The dye fixation value (%F) was calculated using Equation 2 and rounded to the nearest tenth.

$$\%F = \frac{(A_O - A_i)}{A_O} \times 100 \qquad \text{Equation 2}$$

2.8 Colour Fastness Test

Light fastness test was carried out according to the British Standard BS EN ISO 105-B02 (Method 3)[41] using Q-Sun 1000 Xenon test chamber with the irradiance set to 0.65 W/m^2 at the set to temperature of 45°C. The light fastness of the printed wool fabrics was assessed against blue wool scale. Wash fastness test was carried out according to the British Standard BS EN ISO 105-C06:2010 (A1S)[42] using a Mathis WT laboratory wash-test machine. Colour change of the printed samples and the staining of the adjacent fibres were assessed against grey scale.

3 RESULTS AND DISCUSSION

3.1 Microwave Irradiation versus Conventional Heating

The nucleophilic aromatic substitution of tetrachloropyrimidine with substituted amine (dye chromophore) was carried out under microwave irradiation and conventional heating conditions and the results, as shown in Table 1, were compared. As can be seen from Table 1, the reaction rate was enhanced up to 4 folds under microwave irradiation compared with that under conventional heating whereas an improvement in yield was also observed. Using 1:1.1 mmol equivalents of both reactants, the reaction under microwave irradiation reached completion in 90 min with an 84% yield (Scheme 2 and Table 1). These impressive results are attributed to the microwave-absorbing character of the solvent (phosphate buffer-acetone) used for the reaction under microwave irradiation. In the study reported here, acetone, being a polar organic liquid, enhanced the dipole rotation[12,43] and phosphate buffer, being a salt solution, enhanced the ionic conduction[43,44,45] for conversion of microwave energy into rapid and efficient heating resulting in significantly higher rates of reaction with increased yield.

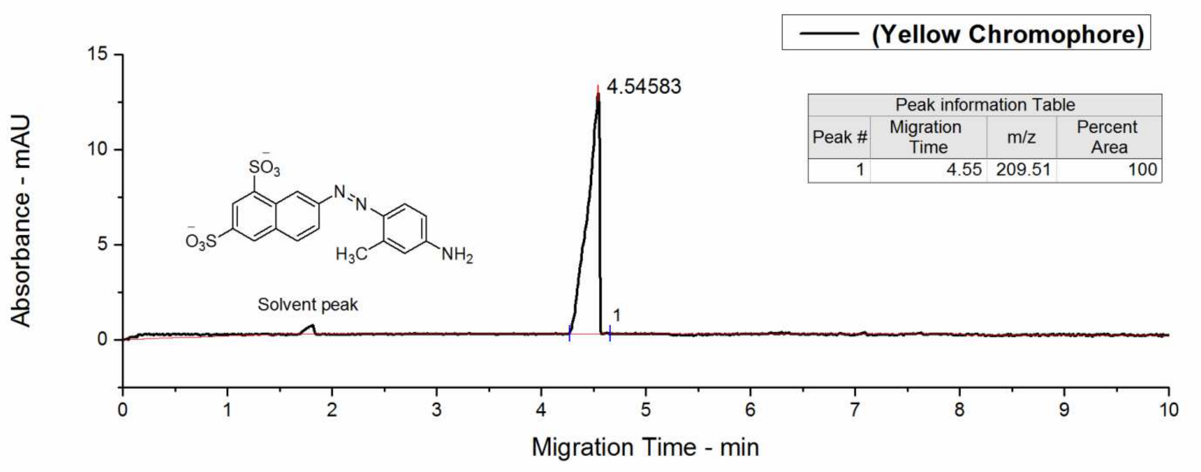
TABLE 1 Comparison of reaction time and yield using microwave irradiation and conventional heating

Dye	Microwave Irradiation		Conventional Heating	
	Reaction Time (min)	Yield (%)	Reaction Time (min)	Yield (%)
Yellow Dye **1**	90	84	360	60

Insert **TABLE 1** here

3.2 Characterisation of Yellow Chromophore and Dye 1 via Microwave Irradiated Synthesis

The MEKC electropherogram of the synthesised yellow dye chromophore **1** at $\lambda_{obs.}$ 420 nm using 20 mM sodium tetraborate, 50 mM sodium dodecyl sulphate (pH 9.3) as eluent buffer is shown in Figure 1. As shown in Figure 1, the synthesised dye chromophore was detected at 4.55 min with percent area of the elution peak being 100% indicating high purity of the synthesised yellow dye chromophore.

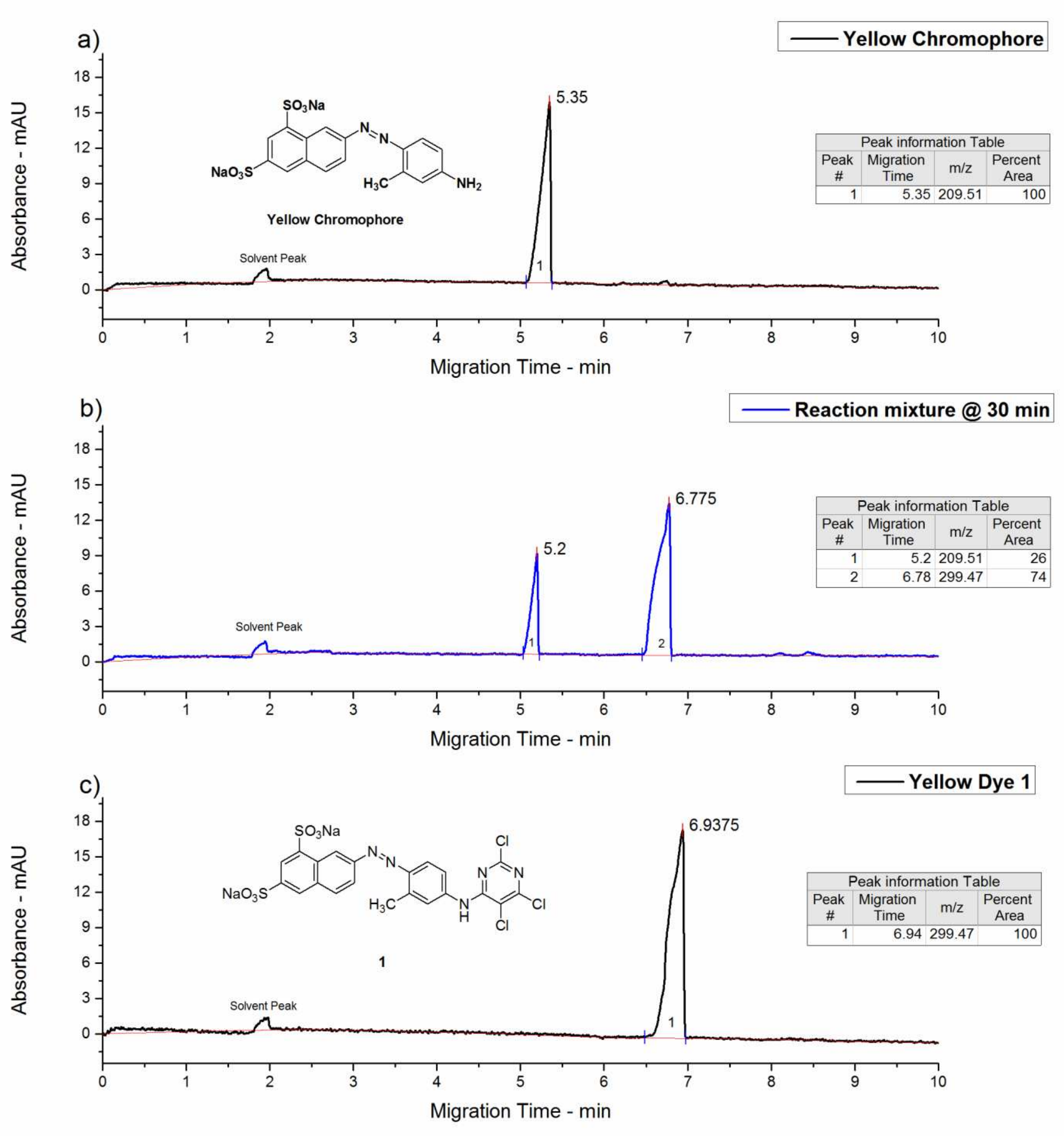


Peak information Table			
Peak #	Migration Time	m/z	Percent Area
1	4.55	209.51	100

FIGURE 1 Electropherogram of yellow chromophore. MEKC conditions: eluent buffer, 20 mM sodium tetraborate, 50 mM sodium dodecyl sulphate (SDS), pH 9.3; pressure injection 0.5 psi over 10 s; voltage 25 kV; detection at 420 nm

Insert **FIGURE 1** here

MEKC electropherogram showing reaction progress and purity of dye, prepared by the microwave irradiation method, is shown in Figure 2(a–c). As can be seen in Figure 2(b), water migrates quickly at the electroosmotic flow (EOF) velocity followed by chromophore (5.2 min) and then yellow dye **1** (6.78 min). This is because that the synthesised dye has an increased molecular weight compared to the chromophore but no additional sulphonate groups that would help increases the solubility of the dye. Moreover, the percent area of the elution peak of dye **1** shown in Figure 2(c) was 100% which indicates that there was no hydrolysed dye in the final product.



Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	5.35	209.51	100

Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	5.2	209.51	26
2	6.78	299.47	74

Peak information Table

Peak #	Migration Time	m/z	Percent Area
1	6.94	299.47	100

FIGURE 2 Electropherograms showing reaction progress and purity of dye **1** (microwave irradiation method). (a) Yellow chromophore; (b) Yellow chromophore - dye **1** after 30 min reaction time; (c) dye **1**. MEKC conditions: Same as those shown in Figure 1.

Insert **FIGURE 2** here

Analysis of FT-IR spectrum shown in Figure 3, suggested that the reddish yellow compound was yellow dye chromophore since IR absorption peaks appeared at 3328 cm^{-1}, 3227cm^{-1} (stretching); 1625 cm^{-1} (bending) and 881 cm^{-1} (wagging), of which all can be attributed the presence of primary amine group on dye chromophore.

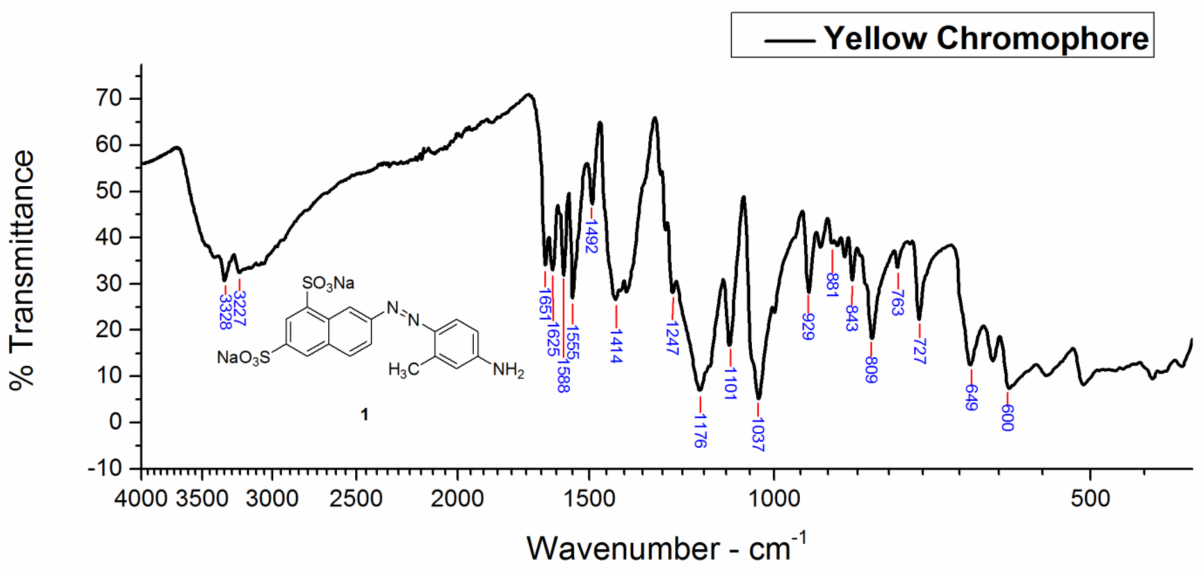


FIGURE 3 FT-IR spectrum of yellow chromophore

Insert **FIGURE 3** here

Analysis of FT-IR spectrum shown in Figure 4 suggested that the compound is dye **1** since peak due to the presence of primary amine in yellow chromophore (Figure 3) at 1625 cm^{-1} is no longer present indicating that the primary amine had successfully reacted with 2,4,5,6-tetrachloropyrimidine. The appearance of new peaks at 1538 cm^{-1} and 1387 cm^{-1} reflect the presence of the C=N group in the dye. Moreover, in accordance with literature,[30,31] the appearance of the peaks at the 1098 cm^{-1} and 849 cm^{-1} [46,47] can be attributed to the stretching vibrations of carbon chlorine bond on the diazine ring of the dye.

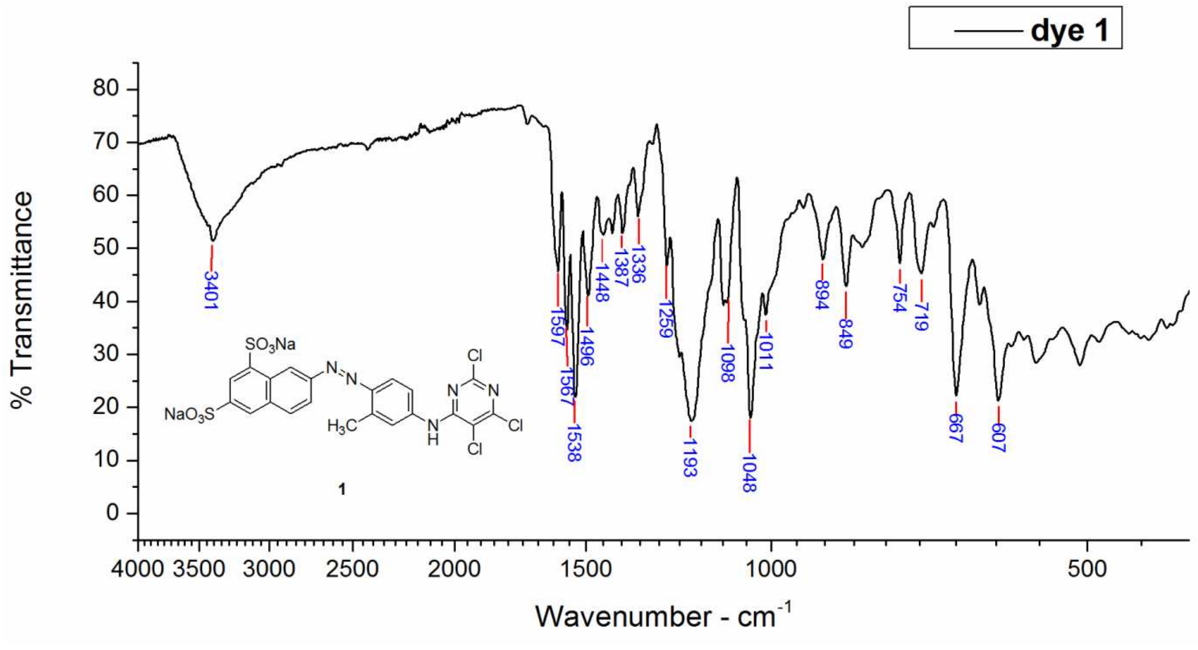


FIGURE 4 FT-IR spectrum of yellow dye **1** synthesised via microwave irradiation method

Insert **FIGURE 4** here

3.3 Printing Properties

The effect of dye fixation conditions (fixation temperature: 102 °C and fixation time: 5 – 25 min at 5 min intervals) on the colour strength and percentage of dye fixation using the synthesised dye **1** to print wool fabric samples are shown in Figure 5. It can be seen, from Figure 5, that the increase in the steaming time from 5 to 15 at 102 °C led to increase in the colour strength and percentage of dye fixation. This may be attributed to the formation of covalent bond between dye **1** and functional groups of wool fibre through nucleophilic aromatic substitution reaction.[48] On the other hand, the decrease in the dye fixation and colour strength beyond 15 min could be due to the hydrolysis of dye **1** under these conditions. Figure 6 presents the digital image of the inkjet-printed wool fabric with prepared reactive ink.

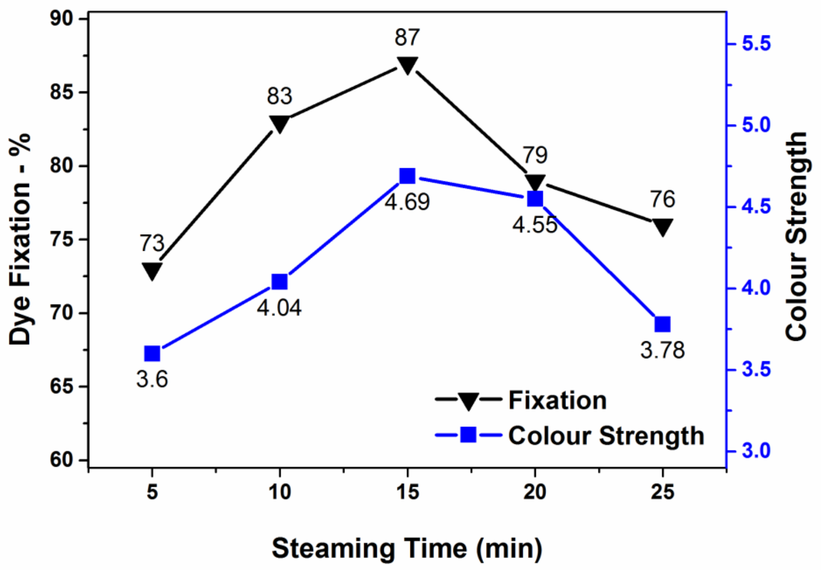


FIGURE 5 Effect of steaming time on the colour strength and dye fixation of prepared ink on inkjet-printed wool fabrics. Fixation conditions: Steaming at 102 °C for 5 – 25 min.

Insert **FIGURE 5** here

FIGURE 6 Digital image of inkjet-printed wool fabric

Insert **FIGURE 6** here

3.4 Colour Fastness Properties

All of the prints for fastness tests were fixed by steaming at 102 °C for 15 min. The colour fastness properties of the reactive ink on wool are listed in Table 2. It can be seen from Table 2 that the printed samples exhibited moderate to very good (6) light fastness. It is believed that the formation of covalent bond between the dye molecule and the fibre facilitates the transfer of energy from the excited state of the dye to the fibre, thus reducing the rate of photodegradation of the dye.[49]

From the wash fastness data shown in Table 2, it can be seen that the printed samples exhibited good to excellent wash fastness rating (4–5), and slight to negligible staining (4–5) on adjacent cotton fabric. The slight to negligible staining obtained for the adjacent cotton is attributable to the removal of unfixed dye from the printed wool fabric during wash fastness testing that then transferred to the adjacent cotton fabric.[50]

TABLE 2 Colour fastness properties of Yellow dye on Wool

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

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

Insert **TABLE 2** here

4 CONCLUSION

The study reported here has shown that chloropyrimidines are sufficiently reactive under microwave irradiation. An effective method for the synthesis of chloropyrimidine based reactive dyes is thus devised. Of paramount importance, the nucleophilic aromatic substitution of tetrachloropyrimidine with amino containing chromophore was achieved in four times shorter reaction time and with modest increase in yield. This finding is significant as it will allow application of highly promising class of reactive dyes in inkjet printing of textiles. In addition, the synthesised dye, when inkjet-printed onto the wool, was able to react with the wool fibre resulting in good colour strength and fixation results. Moreover, all of the samples printed with pyrimidine based yellow ink showed reasonability good light and wash fastness.

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