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Novel sustainable synthesis of dyes for clean dyeing of wool and cotton fibres in supercritical carbon dioxide

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ABSTRACT: A new synthetic route was developed to create an azo-based reactive disperse dye containing the vinyl sulphonyl reactive group. This dye was used to colour wool and cotton fibres using $scCO_2$ as the dyeing medium. The optimum dyeing process was carried out with water pre-treatment at 90 °C and 140 bar during a 60 minute dyeing time. Under optimal conditions, which are relatively moderate for supercritical dyeing processes, the dyed wool fabrics produced uniform dyeings with high colour strength and fastness properties. These wool dyeings provided good colour strength and fixation properties (fixation of 99.4%). Cotton also showed good colour strength results. Crucially, the process did not produce any dyeing effluent. Furthermore, there is a potential to modify a wide scope of disperse dyes using the thiol group via this synthetic method without the need for further purification.

1. Introduction

The traditional methods of dyeing both natural and synthetic fibres have always involved water intensive processes, with an estimated 100 kg of water being required per kg of textiles (Fernandez Cid et al., 2005). Water is a finite resource, and the aqueous dye house effluents contain large amounts of dyestuff in addition to salts and alkali which are required for the colouration of textiles. As pressure on the dyeing industry to become more environmentally friendly and sustainable has increased, the industry has been forced into searching for 'greener' dyeing methods (DeSimone, 2002; Knittel and Schollmeyer, 1995; Montero et al., 2000). One such approach is using supercritical carbon dioxide (scCO_2) to replace water as the dyeing medium. ScCO_2 has been highlighted as an exceptional replacement due to it being non-flammable, cheap, non-toxic, inert and having a relatively mild critical point ($P_c = 73.7$ bar and $T_c = 31.1$ °C).

The dyeing of synthetic fibres in scCO_2 has become well established since 1988 when Schollmeyer et al. first invented the supercritical fluid dyeing (SFD) system (Back et al., 1998; Saus et al., 1993; Schollmeyer et al., 1990). The success of dyeing synthetic fibres is mainly due to the plasticisation effect of scCO_2 on polymers such as polyester (Lewin - Kretzschmar and Harting), which is a phenomenon that improves the mobility of the polymer chains and increases the migration of semi-crystalline polymers. However, in the case of natural fibres which have a higher crystallinity and polarity than synthetic fibres, the inability of the non-polar scCO_2 to swell the polar natural fibres such as wool is a major obstacle in comparison to the dyeing of synthetic fibres (Bach et al., 2002). Additionally, amino and hydroxyl functions of solute molecules are known to reduce solubility in scCO_2 (Draper et al., 2000). Thus, amino groups in wool protein and hydroxyl groups in cotton have a negative effect on the swelling of fabrics. Because the natural fibres cotton and wool are two of the most important textile materials for clothing, the inability to apply the $scCO_2$ dyeing for natural fibres has become a stumbling block for the adoption of the technology by the textile dyeing industry. Hence , the dyeing of natural fibres such as cotton, wool and silk in the alternative dyeing medium is known to be challenging.

A number of methods for dyeing wool and cotton fibres in $scCO_2$ have been proposed in the literature during the last two decades. Mordant dyes, having chelating ligand properties for wool dyeing have been used in supercritical carbon dioxide. These showed good results with excellent wash fastness on dyed fabrics (Guzel and Akgerman, 2000). Researchers found that it was possible to dye wool and cotton fabrics in $scCO_2$ using traditional disperse dyes without any pre-treatment, but the colour strength of the dyed fibre was unsatisfactory for cellulosic fabrics and the wool and cotton fabrics were damaged by the extreme dyeing conditions (Gao et al., 2015; Schmidt et al., 2003; Zheng et al., 2017). A reverse micellar dyeing system applied for dyeing wool and cotton was also reported (Jun et al., 2005; Sawada and Ueda, 2004). Conventional acid dyes were used in this water-pool system in $scCO_2$ dyeing that was regarded as low liquor ratio dyeing with highly concentrated dye solution (Sawada and Ueda, 2004). Fabrics dyed under relatively milder conditions (45-55 °C, 140-160 bar), produced some promising results, providing strong colouration on dyed samples. However, apart from the mixed results in the dyeing of natural fibres, the main factor holding back reverse micellar systems from industrial applications is the use of surfactants (Lewin-Kretzschmar and Harting, 2004). The surfactants used are often harmful to the environment, having a low biodegradability. At present, there does not seem to be an efficient method to remove the surfactants from the dyed fabric, consequentially losing the advantage of the ease of recycling the $scCO_2$ (Sawada and Ueda, 2007).

One of the more promising concepts that could overcome the limitation of the mentioned procedures is the use of $scCO_2$ soluble disperse dyes that have been modified with a highly reactive functional group (Banchero, 2013). These dyes, known as reactive disperse dyes, are able to form covalent bonds with the hydroxyl or amine groups present on the natural fibres, resulting in strong fixation of the dye to the fibre. The general method of designing reactive disperse dye structures involves modifying traditional disperse dye structures with reactive groups. The structures of the reactive disperse dyes are typically based on the azo-benzene or anthraquinone chromophores due to their strong colour strength and versatility when modifying solubilising power and reactive functionality. One major advantage of using such dyes is that they are non-polar and potentially soluble in $scCO_2$. Many different reactive groups have been reported for dyeing natural fibres. Initially, a few common reactive functional groups such as triazine, bromoacrylic acid and halogenated acetamide were utilised to modify different disperse dyes (Fernandez Cid et al., 2005; Gao et al., 2014; Long et al., 2012; Özcan et al., 1998; Van der Kraan et al., 2007; Yang et al., 2017). Relatively good high fixation and colouration dyeing results were obtained. Nevertheless, to achieve the quality of dyeing observed, high pressure, temperature, extensive time (higher than 200 bar, 100 °C, 120 mins, respectively) and additives such as a phase transfer catalyst and co-solvent were required.

The objective of this study was to find a general synthetic route to synthesise azo-based disperse dyes containing the vinyl sulphonyl reactive group, and apply them in a natural fabric dyeing procedure using the eco-friendly supercritical technology to produce excellent dyeing properties on natural fabrics. Reactive dyes containing the vinyl sulphonyl group can be used in conventional dyeing for cotton without alkali, and have a great potential to be applied in the supercritical dyeing (Koh et al., 2003). Amino groups on the side chains of the amino acids in wool fabric and hydroxyl groups in the cotton cellulose are reactive to the vinyl sulphonyl reactive dyes under a wide range of conditions (Lewis, 1982). Vinyl sulphonyl reactive disperse dyes have been synthesised for the supercritical dyeing of natural fabrics (Liao et al., 2000b; Long et al., 2012; Van der Kraan et al., 2007). This paper provides a new and simple route to synthesise a vinyl sulphone modified disperse dye without further purification in the whole process, which is also potentially suitable for industrial scale production. The dyeing process using this vinyl sulphonyl dye was carried out under relatively mild conditions, which it has been suggested uses only half of the energy of current processes on an industrial scale (Group).

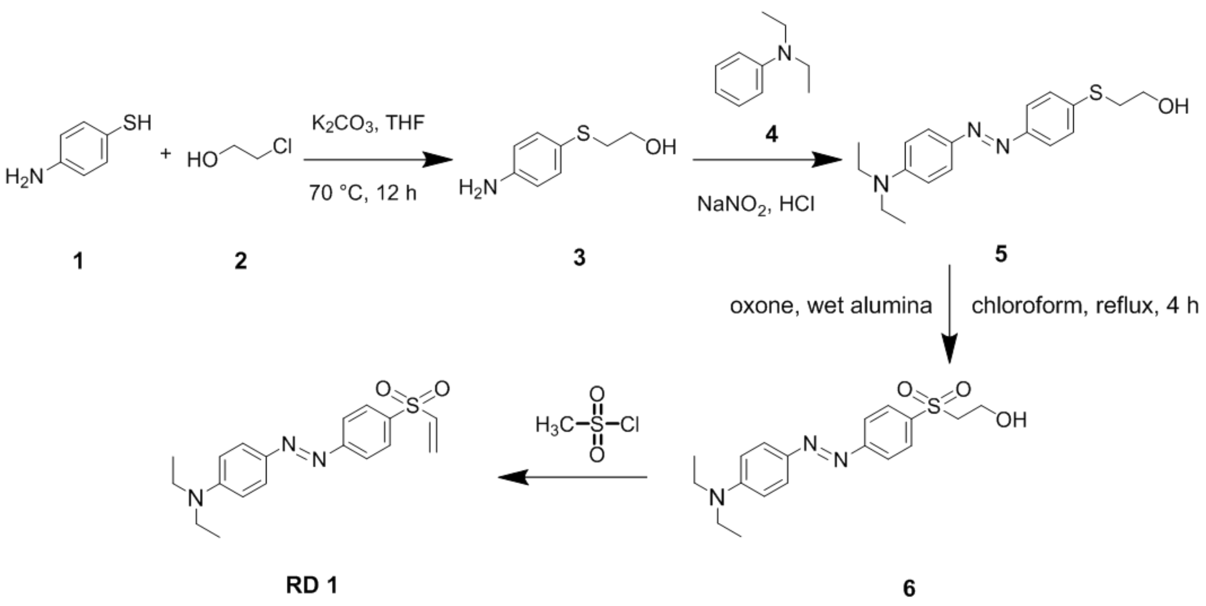
2. Experimental

2.1 Materials

All solvents were HPLC grade. Pure carbon dioxide gas (99.6 vol %) was used for the supercritical carbon dioxide dyeing of fabrics. 4-Aminobenzene-1-thiol was purchased from Fluorochem Ltd. 2-Chloroethanol was purchased from Merck KGaA. N,N-diethylaniline, cyanuric chloride and methanesulphonyl chloride were purchased from Argos Organics. The sourced, bleached and unmercerised fabrics (the density of cotton fabric was 119 g m^{-2}, the density of wool fabric was 131 g m^{-2}) were kindly provided by Whaleys (Bradford) Ltd., UK.

2.2 Dye preparation

The synthetic route given in Scheme 1 provides a general method to synthesise the vinyl sulphone based reactive disperse dye. The synthesis utilises an efficient coupling reaction through the use of starting reagents with simple chemical structures, providing increased versatility compared to previous synthetic methods found in the literature (Koh et al., 2003). In this study, the target reactive disperse dye (RD 1) modified with a vinyl sulphonyl group was synthesised, starting from the coupling component aniline which contained a thiol group. The corresponding sulphide was obtained through the addition of chloroethanol. To form the azo disperse dye, the sulphide was coupled to N-N-diethylaniline, which proved to be an appropriate nucleophile in the electrophilic aromatic substitution, due to the mesomeric effect present within the molecule. The sulphone was obtained successfully by oxidation, with the final step forming the vinyl sulphonyl reactive group. Methanesulphonyl chloride was used to induce elimination of the hydroxyl group. In the presence of a base, the vinyl sulphonyl disperse dye was produced via elimination. In contrast to the synthesis of traditional reactive dyes, reactive disperse dyes are mainly synthesised in non-aqueous conditions. The whole procedure was carried out without further purification after each step (see the experimental and characterisations in the Supporting Information).



Scheme 1. Synthetic route of the 4-[2-[4-(ethenylsulphonyl)phenyl]diazenyl]-N,N-diethylbenzenamine (RD 1).

2.3 Supercritical CO_2 system

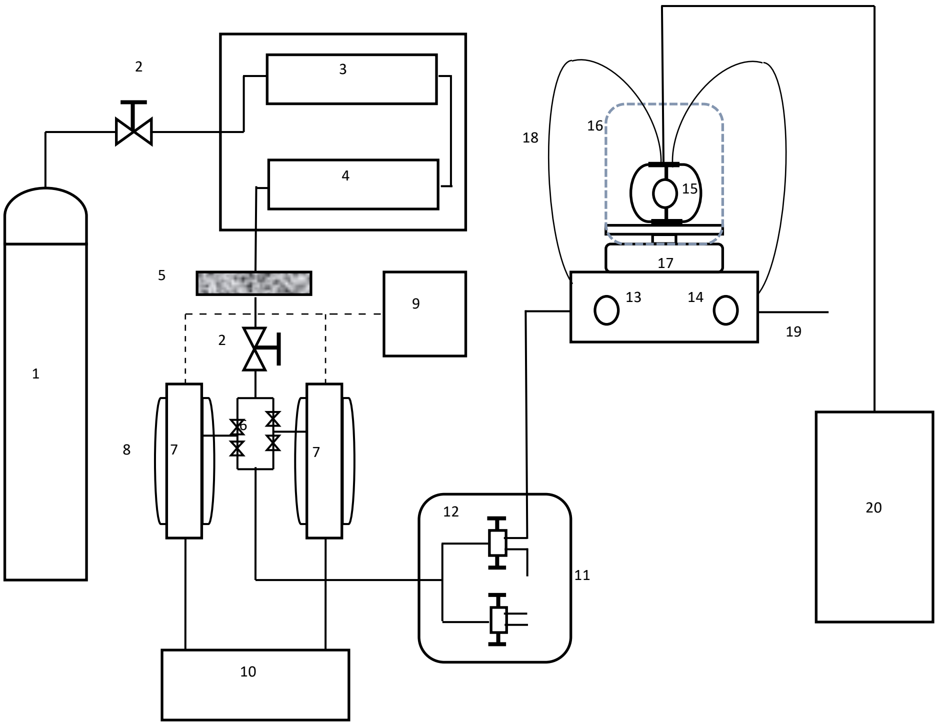


Fig. 1. Schematic diagram of the lab scale plant for fabric dyeing in supercritical carbon dioxide: (1) cylinder; (2) stop valves; (3) H_2O scavenger; (4) O_2 scavenger; (5) filter; (6) electronically controlled valves; (7) syringe pumps (Isoc 260D); (8) cooling jacket; (9) chiller; (10) pump controller; (11) central control panel; (12) high pressure valves; (13) inlet valve; (14) outlet valve; (15) high pressure view cell; (16) polycarbonate shield; (17) stirrer hotplate; (18) tubing; (19) outlet tubing; (20) pressure display and temperature control.

The Wolfson CO_2 Laboratory at the University of Leeds provided the high pressure equipment that was used for the dyeing experiments in scCO_2. The apparatus was built around a 20 mL high pressure view cell, which was previously designed and made by researchers at the University of Leeds. The cell was easy to disassemble and had a body and a lid. Two 15 mm thick borosilicate glass windows were installed, one in the body and the other in the lid, providing visualisation through the whole cell. The cell had an inlet, outlet and thermometer connection on the top. The cell was placed on a stirrer hotplate that provided heating and stirring. Fig. 1 shows the components of the laboratory scale plant for supercritical dyeing.

2.4 General dyeing procedure in supercritical carbon dioxide

2.4.1 Water pre-treatment

Water pre-treatment of the fabrics was carried out at room temperature for 30 minutes. An excess quantity of 3 % on mass of the fibre (omf) water was used to penetrate the fabric in order to guarantee that most of the water was still available after 30 minutes of evaporation. For example, when 30 % omf of water was used to pre-treat a piece of fabric, 33 % omf of water was added initially. After 30 minutes, around 3 % omf of water had evaporated from the fabric at room temperture. The amount of water that remained on the fabric after pre-treatment was weighed before dyeing.

2.4.2 Supercritical dyeing procedure

A piece of fabric (100 ± 0.1 mg) was placed at the bottom of the cell together with 5 % omf of fine dye powder and a stirrer bar. The cell was rinsed by injecting gaseous CO_2 for 2 minutes in order to remove residual air. After the cell was sealed, the system was pressurised to 40 bar with CO_2 using a pair of Isco 260D syringe pumps. The heating was turned on and the temperature was set. Once the desired temperature was reached, the pressure was increased slowly to 140 bar by injecting further CO_2. Heating was stopped when the dyeing process finished after a fixed dyeing time. The reactor was depressurised by gradually opening the outlet valve. Once the cell cooled down to room temperature, it was then opened and the sample retrieved for analysis.

2.5 Colour analysis

The colour strength of an object is described by the K/S value of the scCO_2 dyed natural fabric, which is determined by the Kubelka–Munk equation (Eq. 1). Here K and S are spectral absorption and scattering coefficients respectively. R_{min} is the minimum value of the reflectance curve, determined by measuring the dyed fabric with a Minolta spectrophotometer (model CR3600d; Minolta Co., Japan) (Lewis and Vo, 2007).

$$K/S = (1 - R_{min})^2/2R_{min}$$

Eq. 1. Kubelka-Munk equation (Lewis and Vo, 2007).

The K/S value at R_{min} is directly proportional to the loading of dye on the substrate. The integral value f_k, is used as a more accurate expression of relating dye concentration to the colour intensity of an opaque surface. These results may be correlated better with the visual evaluation of the sample rather than the sum K/S. The definition of f_k is the sum of the weighted values in the visible region of the spectrum, as shown in Eq. 2. Here λ, is wavelength.

$$f_{k(dyed)} = \sum_{\lambda=400}^{700} (K/S)_{\lambda}$$

Eq. 2. Definition of f_k value (Lewis and Vo, 2007).

Each sample was stripped of unfixed dye by Soxhlet extraction with a 50 wt. % solution of acetone : water (1 : 1) in water for 30 min. The f_k value of the extracted textile $f_{k(extr)}$ was determined and used to calculate the percentage of dye molecules that were fixed to the textile, namely fixation (F) (Eq. 3):

$$F = \left(f_{k(extr)}/f_{k(dyed)}\right) \times 100\%$$

Eq. 3. Definition of F value (Lewis and Vo, 2007).

2.6 Fastness

Colour fastness to washing, light and rubbing of the prepared dyes on the wool and cotton fabrics were investigated according to the standard methods for the assessment colour fastness of textile (Palmer, 2010). Colour assessment was carried out under standardised lighting conditions (D65), in a dark room.

2.7 Microscopic study

In order to have a better understanding of the effect of $scCO_2$ on the surface physical properties of the dyed fabric, a scanning electron microscopic (SEM) study was carried out. SEM is a widely used technique. In this method, a focused beam of electrons is scanned across the surface of an electrically conductive specimen. A Jeol JSM-6610LV model SEM was used for the study. The sample preparation involved the deposition of a representative amount of the sample fabric onto a standard SEM stub using carbon-conductive tape. The dyed fibre sample was then gold-coated using a Bio-Rad SC500 diode sputter coating unit. The sample was examined under the electron microscope over the magnification range of x 200 to x 15000, using an accelerating voltage ranging from 5 kV through to 30 kV.

3. Results and discussion

One of the major advantages that is particularly relevant to carrying out dyeing in $scCO_2$ is the ability to have fine control over solvent properties such as density, by changing the temperature and pressure of the system.

According to previous studies (Abou Elmaaty and Abd El-Aziz, 2017; Banchero, 2013), greater pressures led to better dyeing results when the synthesised reactive disperse dyes were used in the dyeing system. Because the density of carbon dioxide greatly increased as it was compressed, the dye was dissolved more effectively as the pressure was increased (Banchero, 2013; Liao and Chang, 2012; Liao et al., 2000a). Dyes absorbed by the fibres would not migrate back to the carbon dioxide phase easily because of the formation of the covalent bonds between dyes and fibres. Previous research was carried out under high pressure (>200 bar). In order to alleviate the burden of these high pressures on industrial feasibility and equipment costs etc., all experiments in this study were conducted under milder conditions (140 bar).

In the previous work (Long et al., 2011; Long et al., 2012; Van der Kraan et al., 2007), water pre-treatment and water addition were shown to improve the dyeing results dramatically. The dyeing time and temperature had great impact on the dyeing qualities (Bach et al., 2002). Thus, in this study, the amount of water, dyeing time and temperature was quantified in order to establish the best dyeing conditions of the RD 1.

3.1 Dyeing wool fabric using RD 1 containing the vinyl sulphonyl group

3.1.1 Investigation of the effect of water pre-treatment on the dyeing of wool, using the RD 1 containing the vinyl sulphonyl reactive group

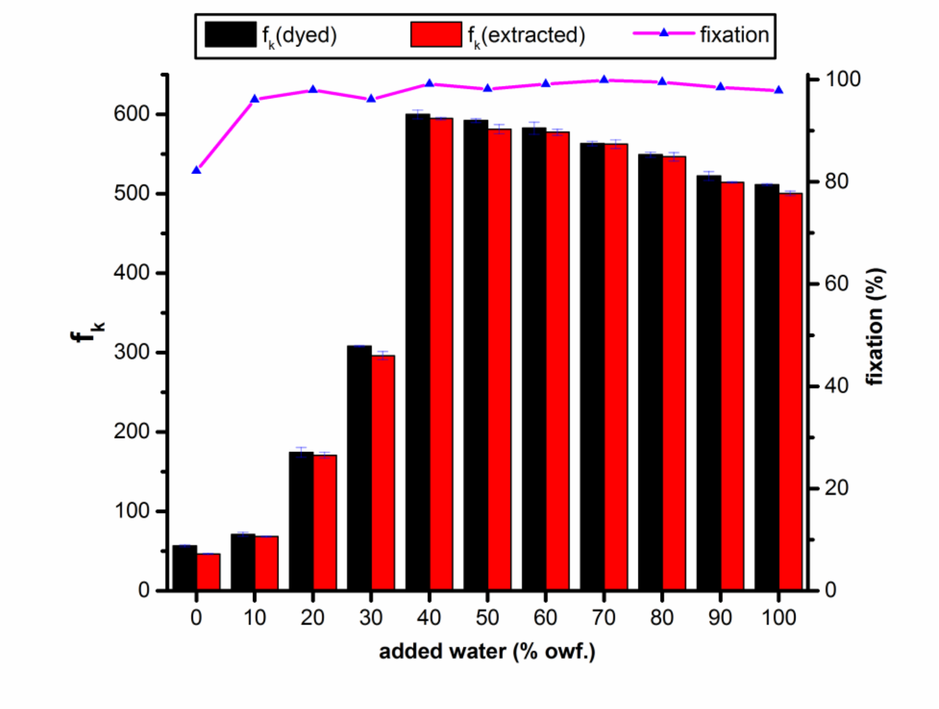


Fig. 2. Effect of water pre-treatment on wool fabric on the f_k value and the dye fixation of wool dyed in $scCO_2$ with 5 % omf of RD 1 at 90 °C, 140 bar for 60 minutes.

As the aim of supercritical dyeing is to reduce the huge amount of water that is used during the conventional dyeing processes, the initial supercritical dyeing experiments used a little water in the pre-treatment to improve the fibre accessibility. To figure out the optimal amount of water in the dyeing, a series of experiments was carried out at 140 bar, 90 °C, with 5 % omf of RD 1 and different amounts of water during a 60 minute period.

As seen in Fig. 2, poor dyeing quality was observed if no water pre-treatment was used. However, with the pre-treatment of water, the colour depth increased significantly up to $f_{k(dyed)}$ values of 599.7 at 40 % omf of water addition compared to that obtained with non-pre-treatment ($f_{k(dyed)} = 56.5$). The slight decrease in the f_k value after 40 % omf can be attributed to either the competitive reaction between water and the reactive dye, or the increasing density of the supercritical fluid due to the additional water, which would lead to a lower solubility of the synthesised reactive disperse dye. Excellent fixation rates ($F > 96.0$ %) were obtained after adding only 10 % omf of water. The greatest fixation rate of 99.4 % was obtained when wool was dyed with 70 % omf of water addition in this series. The investigation into water-pre-treatment proved that water plays an important role in the dyeing process. One of the possibilities for the positive effect of water on the dyeing process is the increase in the solubility of the dye in $scCO_2/H_2O$ due to the water pre-treatment. The small addition of water possibly allowed the reaction to occur in a relatively homogeneous phase, leading to a boost in the dyeing quality. Another fact is that water acts as a swelling reagent for the hydrophilic textiles, allowing the dye to diffuse inside the fibre (Van der Kraan et al., 2007). The alkali-free dyeing process would enable the problem of dye hydrolysis to be significantly reduced (Weber and Stickney, 1993). Moreover, the high temperature which had the ability to achieve the dye-fibre covalent bonding without adding alkali could help to boost the reaction between the dye and the fibre. Thus, when sufficient dye was provided in the process, the impact of hydrolysis of the dye on the dyeing results was eliminated (Lewis and Vo, 2007).

3.1.2 Investigation of the effect of the temperature on the dyeing of wool, using the RD 1 containing the vinyl sulphonyl reactive group

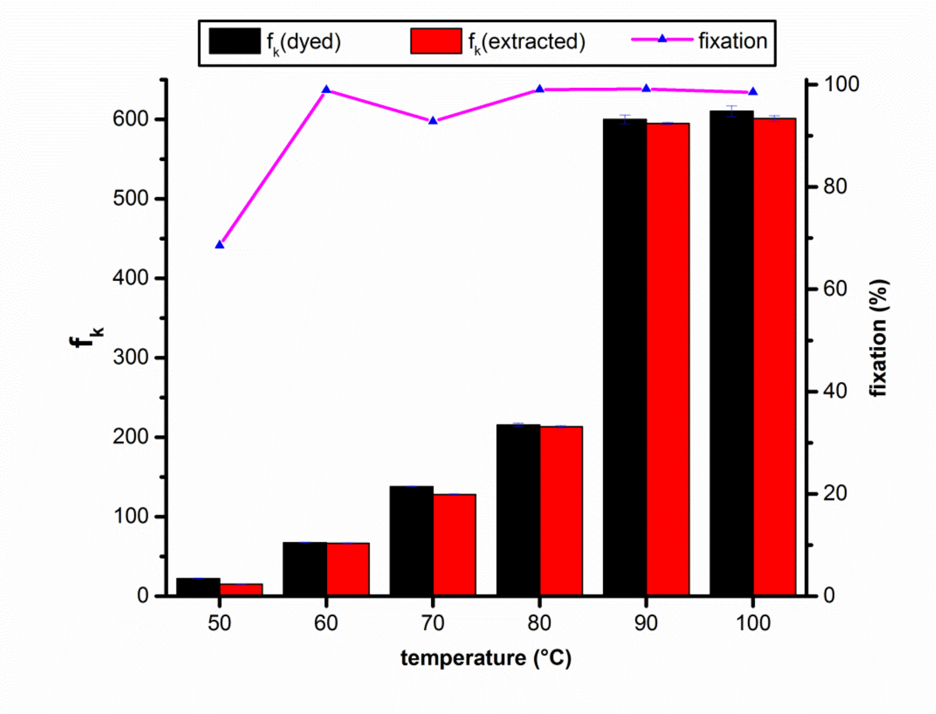


Fig. 3. Effect of temperature on dye fixation of wool fabric and the f_k value of wool dyed in $scCO_2$ with 5 % omf of RD 1 and 40 % omf of pre-treatment water, at 140 bar, for 60 minutes.

In the previous study of the effect of water pre-treatment, the best dyeing quality was obtained with fabrics containing 40 % omf of water addition in the $scCO_2$ dyeing system. Subsequently, the influence of temperature on the effectiveness of wool dyeing was investigated using different temperatures at 140 bar with 5 % omf of synthesised RD 1, with the fabric containing 40 % omf of water during a 60 minute dyeing period.

As seen in Fig. 3, a significant improvement in the extent of fixation was observed when the dyeing temperature was increased from 50 °C (F = 68.5 %) to 60 °C (F = 97.2 %). The fixation rates remained higher than 90 % for the temperatures ranging from 60 °C to 100 °C. The fixation data demonstrated that the dye had very low reactivity with wool fabric below 60

°C. Moreover, the f_k value linearly increased when the temperature was increased from 50 °C ($f_{k(dyed)}$ = 21.9) to 80 °C ($f_{k(dyed)}$ = 215.2). Desirable colour strength was achieved at 90 °C ($f_{k(dyed)}$ = 599.7) and 100°C ($f_{k(dyed)}$ = 610.2), mainly due to the increase in diffusivity and decrease in viscosity, which allowed for better mass transport by increasing temperature at constant pressure.

3.1.3 Investigation of the effect of dyeing time on the dyeing of wool, using the RD 1 containing the vinyl sulphonyl reactive group

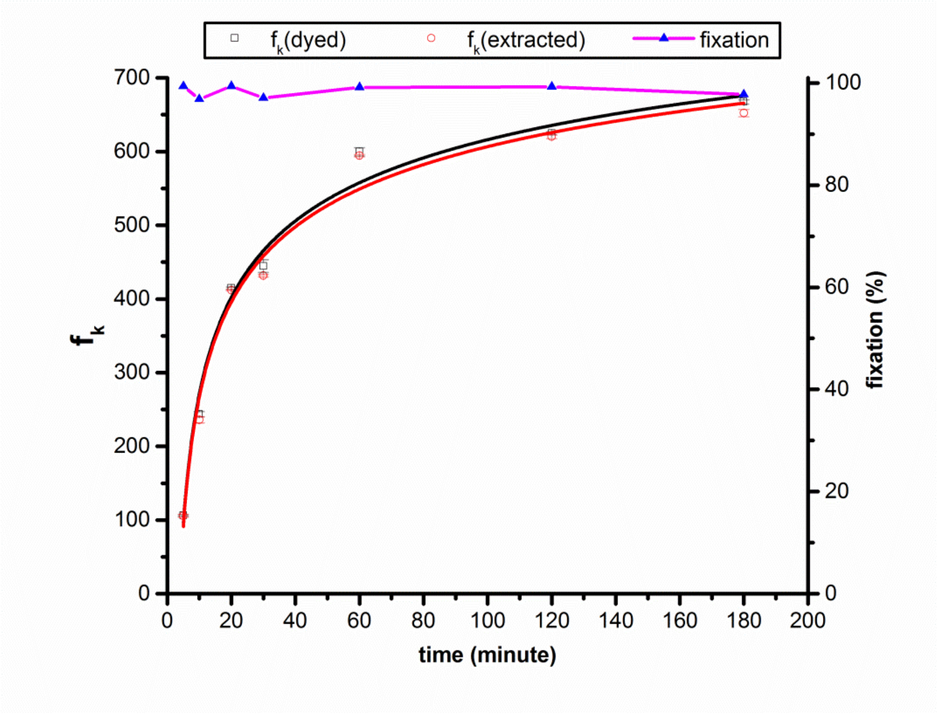


Fig. 4. Effect of dyeing period on dye fixation of wool fabric and the f_k value of wool dyed in $scCO_2$ with 5 % omf of RD 1 and 40 % of omf water in the pre-treatment process at 90 °C, 140 bar.

Dyeing times of 60 minutes were first applied with the synthesised RD 1. However, when considering the scale-up of the waterless dyeing process to an industrial scale, different dyeing times would need to be considered. Experiments varying the dyeing time were undertaken in order to investigate the viability of different process times. The optimum conditions aforementioned (90 °C and 140 bar) were chosen for this series of experiments.

In Fig. 4, increasing the dyeing time significantly enhanced the dyeing qualities. Remarkably, within 20 minutes an $f_{k(dyed)}$ value of 414.7 was already measured in the dyed piece of wool. A slight improvement was observed after 60 minutes of dyeing time. The darkest orange colour ($f_{k(dyed)} = 667.5$) was obtained at the dyeing time of 180 minutes in this series. Most importantly, it was found that not only high dye fixation rates ($F > 96.0$ %) were achieved, but also the fixation rates were independent of the dyeing period (after more than 5 minutes dyeing period). The nucleophilic addition reaction between vinyl sulphonyl groups and wool fibre occured within 5 minutes under these dyeing conditions.

3.1.4 Colour fastness test

Table 1. The fastness data of wool fabrics coloured with 5 % omf of dye, 40 % omf of water in scCO$_2$ at 90 °C, 140 bar during different dyeing periods.

Dyeing time (mins)	Wash fastness							Rub fastness		Light fastness
	Fading	Staining						Dry	Wet	
		Acetate	Cotton	Nylon	PET	Acrylic	Wool			
10	5	5	5	4-5	5	4-5	5	5	4-5	5-6
20	5	5	5	4-5	5	5	5	5	5	5-6
60	5	5	5	5	5	5	5	5	5	5-6
180	5	5	5	5	5	5	5	5	5	5-6

The wash fastness of wool fabrics coloured with 5 % omf of dye, 40 % omf of water, pretreated at 90 °C and 140 bar was tested at various dyeing times (Table 1). All wool samples were extracted with a 50 wt. % solution of acetone in water before the wash fastness was assessed. Superior fading fastness data was displayed due to the removal of all unreacted dyes with the acetone : water (1 : 1) solution on dyed fabrics, which achieved the requirements of a commercial product. However, the staining fastness rate was slightly less than the fading fastness, especially for samples treated at insufficient dyeing times. Excellent wet and dry rub fastness of the dyed wool fabrics were obtained. Moreover, good light fastness rated 5-6 was also obtained for the wool fabrics with different dyeing times.

3.2 Dyeing cotton fabric using RD 1 containing the vinyl sulphonyl group

3.2.1 Investigation of effect of water pre-treatment on the dyeing of cotton, using the RD 1 containing the vinyl sulphonyl reactive group

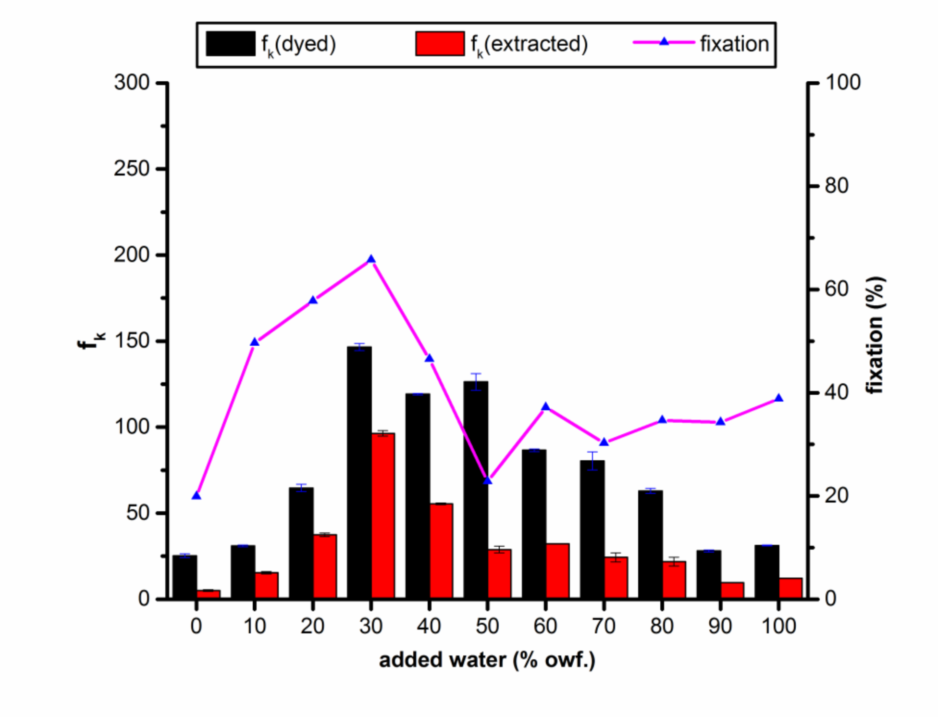


Fig. 5. Effect of water pre-treatment (on cotton fabric) on the f_k value and the dye fixation of the dyed cotton in scCO$_2$ with 5 % omf of RD 1 at 90 °C, 140 bar for 60 minutes.

The investigation into the effect of the parameter range for the water pre-treatment of cotton was carried out under the different conditions as for the wool dyeing experiments.

In Fig. 5 the colour depth increased initially and reached a maximum value ($f_{k(dyed)}$ = 126.3) at 30 % omf of water addition before decreasing. Moreover, the hydrophobic, synthesised RD 1 showed little affinity for cotton fibre and relatively low solubility in pure scCO$_2$, resulting in a low dye fixation (F = 19.9 %) without any water pre-treatment. Pre-treatment of the fabric with water helped to improve the solubility of dyes in $scCO_2$ and the swelling of fibre, resulting in fixation rates increasing up to 65.8 % after 30 % omf of water addition (Patel and Patel, 2011). A drop in the fixation rates was observed above this 30 % value before it eventually stabilised (when the F value was around 35 %) when the amount of water was increased up to 100 % omf.

As was observed with wool, water pre-treatment greatly affected the dyeing qualities of the cotton.

3.2.2 Investigation of the effect of the temperature on the dyeing of cotton, using the RD 1 containing the vinyl sulphonyl reactive group

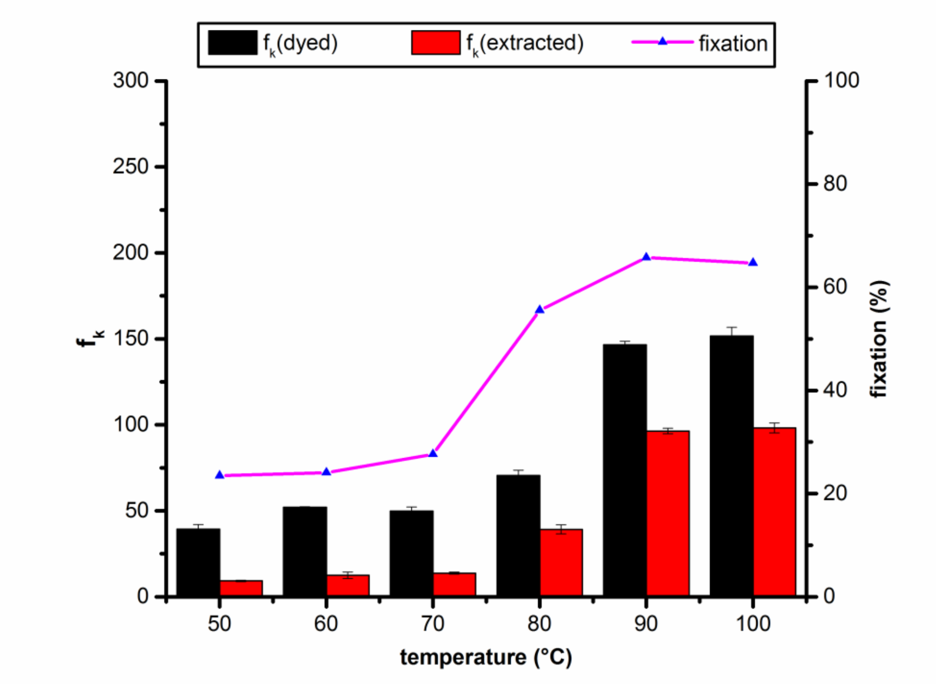


Fig. 6. Effect of temperature on dye fixation of cotton fabric and the f_k value of cotton dyed in $scCO_2$ using 5 % omf of RD 1 and 30 % omf of water, at 140 bar, for 60 minutes.

The experimental setup involving $scCO_2$ was designed to operate at 140 bar for a 60 minute dyeing time. Based on the results of the optimum amount of water addition, cotton was pretreated with 30 % omf of water for 30 minutes before the dyeing experiments were carried out. The results are shown in Fig. 6.

The f_k value of the dyed cotton remained steady and relatively low until a temperature of 80 °C was reached. The colour depth clearly increased with temperature. The f_k value almost doubled when the temperature was increased from 80 °C to 90 °C. A considerable improvement of fixation was observed (from 27.6 % to 65.8 %) when the temperature was increased from 70 °C to 90 °C. The reactivity of the dye was enhanced dramatically from 70 °C to 80 °C, due to the large increase in the fixation, which suggests that more covalent bonds were formed with the temperature increase. The increase of the f_k value from 80 °C to 90 °C was primarily due to the greater diffusivity. Beyond 90 °C, the colouration and the fixation remained constant, which demonstrated that the effectiveness of dyeing reached a maximum at approximately 90 °C.

3.2.3 Investigation of the effect of the dyeing time on the dyeing of cotton, using the RD 1 containing the vinyl sulphonyl reactive group

In this series of experiments, the dyeing system was maintained at 140 bar, and 90 °C. The cotton fabric was pre-treated with 30 % omf of water. Fig. 7 shows the surprising result that the fixation reached up to 61.7 % after only 30 minutes of dyeing. Moreover, the f_k value increased rapidly to 146.6 within 60 minutes. The dyeing results were generally improved with time, indicating that the dyeing was completed after around 60 minutes.

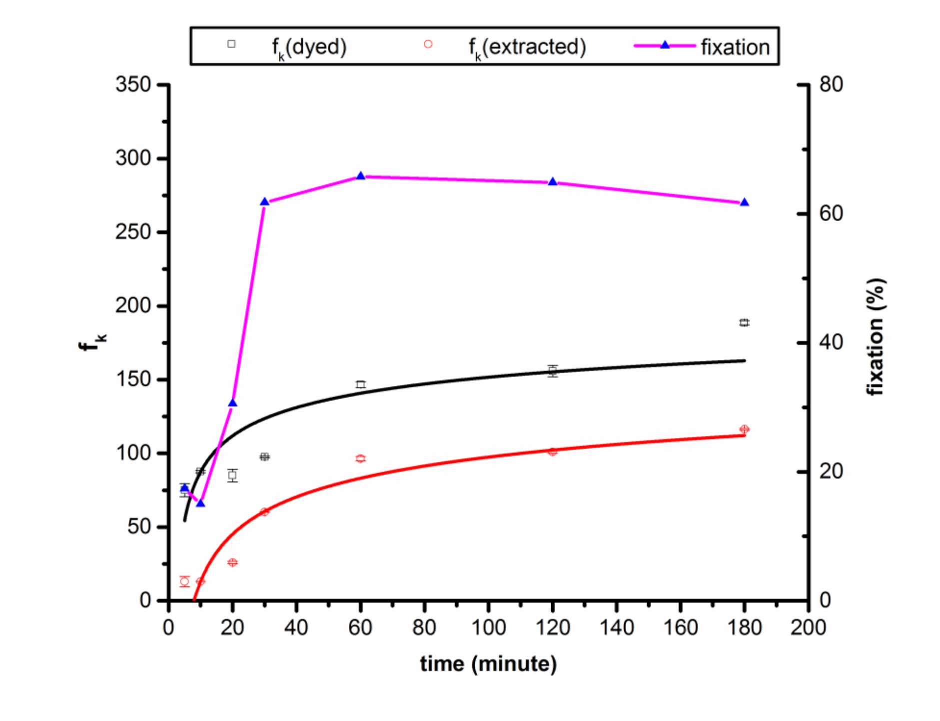


Fig. 7. Effect of dyeing time on the dyeing of cotton fabric with respect to the f_k value and on the dye fixation of dyeing cotton in scCO$_2$ with 5 % omf of RD 1 at 90 °C, 140 bar.

3.2.4 Colour fastness test

Table 2. The fastness data of cotton fabrics coloured with 5 % omf of dye, 30 % omf of water in scCO$_2$ at 70 °C, 140 bar at different dyeing times.

Dyeing time (mins)	Wash fastness							Rub fastness		Light fastness
	Fading	Staining						Dry	Wet	
		Acetate	Cotton	Nylon	PET	Acrylic	Wool			
10	4	3-4	4	3	3-4	3-4	3	4	3-4	5-6
20	5	4	5	4-5	3-4	3-4	4	4	3-4	5-6
60	5	5	5	5	5	4-5	5	4-5	3-4	5-6
180	5	5	5	5	5	4-5	4	4-5	4	5-6

Table 2 summarises the fastness properties of the scCO$_2$-dyed cotton fabrics using the previously identified temperature and water pre-treatment conditions and at different dyeing times. Generally, once the surface dye was removed, dyeing of satisfactory wash fastness was achieved. It can be seen that the dyeing time had a significant effect on the fastness properties, with the fading fastness increasing as the processing time increased. Regarding the staining fastness, a general consensus that an increase in processing time resulted in improved stain fastness was not observed. Dry rub fastness of the dyed cotton rated 4 or 4-5 were obtained. Wet rub fastness rate of the dyed cotton were slightly less than the dry one. The light fastness of dyed cotton fabrics presented moderate to very good (5-6) fastness properties for the synthesised dyes.

3.3 Microscope study

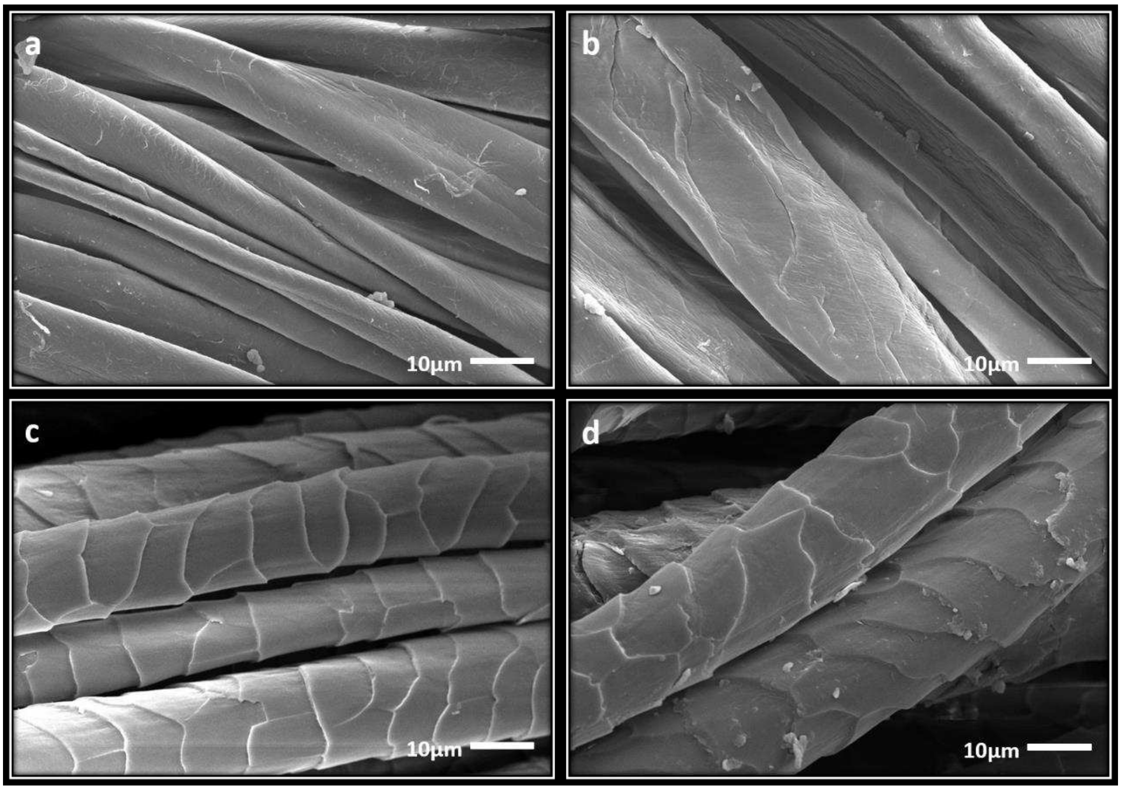


Fig. 8. SEM images of fabrics. Microscopy studies were undertaken to identify (a) supplied cotton fibres; (b) dyed cotton fibre; (c) supplied wool fibres; (d) dyed wool fibre. Dyeing conditions: cotton-90 °C, 140 bar, 3 % omf of dye, 30 % omf of water pre-treatment, 60 minutes dyeing time; wool-90 °C, 140 bar, 5 % omf of dye, 40 % omf of water pre-treatment, 60 minutes dyeing time.

Microscopy studies were undertaken to establish whether or not the process conditions damaged the fibres. Fig. 8 demonstrates that the control cotton fibres and wool fibres have a smooth surface. It is apparent that apart from some particles appearing, no clear split or fibrillation was observed on the surface of either the cotton or the wool fibres after dyeing (Fig. 8b, Fig. 8d) compared to the control fibres, (Fig. 8a, Fig. 8c). This indicates that the relatively moderate dyeing conditions reported do not damage the cotton fibres and wool fibres. Particles found on the surface of the dyed fibres were likely to be a result of oligomer or polymeric dye precipitation.

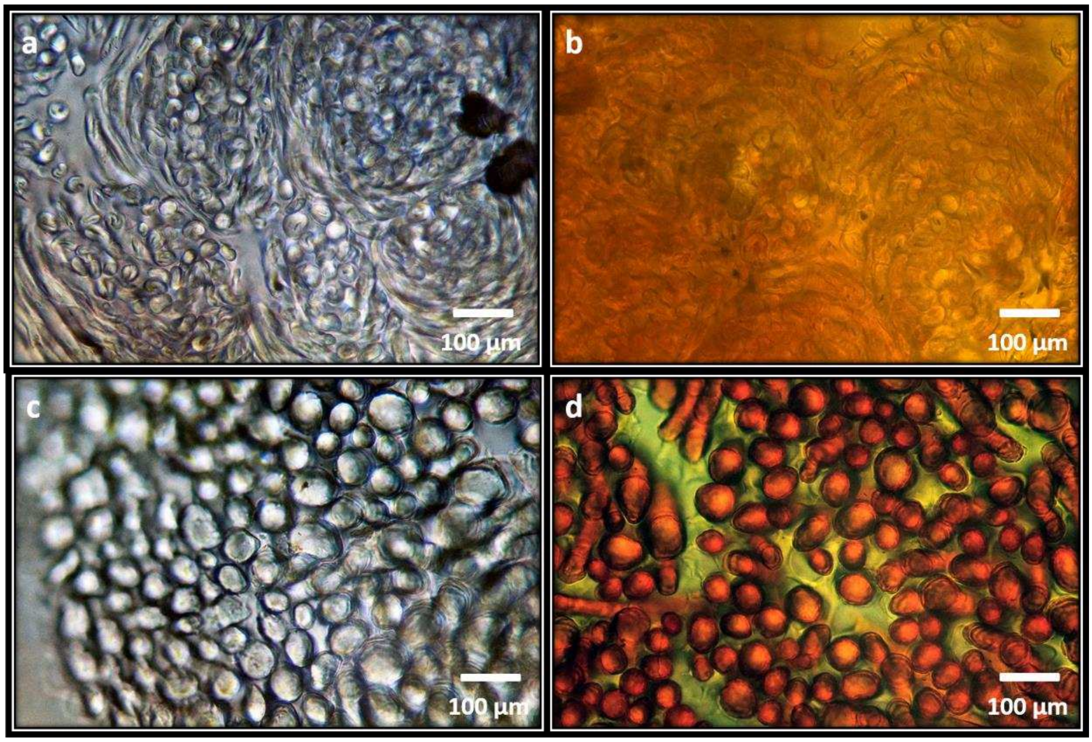


Fig. 9. Cross-section images (a) supplied cotton fibres; (b) dyed cotton fibre; (c) supplied wool fibres; (d) dyed wool fibre. Dyeing conditions: cotton-90 °C, 140 bar, 5 % omf of dye, 30 % omf of water pre-treatment, 60 minutes dyeing time; wool-90 °C, 140 bar, 5 % omf of dye, 40 % omf of water pre-treatment, 60 minutes dyeing time.

Cross-section images of the dyed wool fabrics and the cotton fabrics show that ring dyeing was not observed. A highly effective dye uptake occurred after wool dyeing in $scCO_2$, with cotton dyeing in $scCO_2$ also providing an acceptable dye uptake. Examples are shown in Fig. 9. The individual wool fibre can be observed and was well penetrated by the RD 1 molecules (Fig. 9d). However, there were some lighter areas in Fig. 9b, indicating that an uneven dyeing was achieved for the dyed cotton. The diffusion of dyes in the free volume in amorphous areas is not very fluent due to the hindrance of the hydrogen bonds of cotton. In order to enhance the levelness of dyed cotton, it will be necessary to improve the dye itself, but there is also a need to modify the dyeing equipment; for instance, improving the circulation of the dyeing process.

3.4 Presentation of the Dyed Samples

Fig. 10**Error! Reference source not found.** presents the dyed samples. A: dyed wool sample; B: dyed wool sample extracted with acetone : water (1 : 1); C: dyed wool sample washed with water; D: dyed cotton sample; E: dyed cotton sample extracted with acetone : water (1 : 1); F: dyed cotton sample washed with water and detergent.

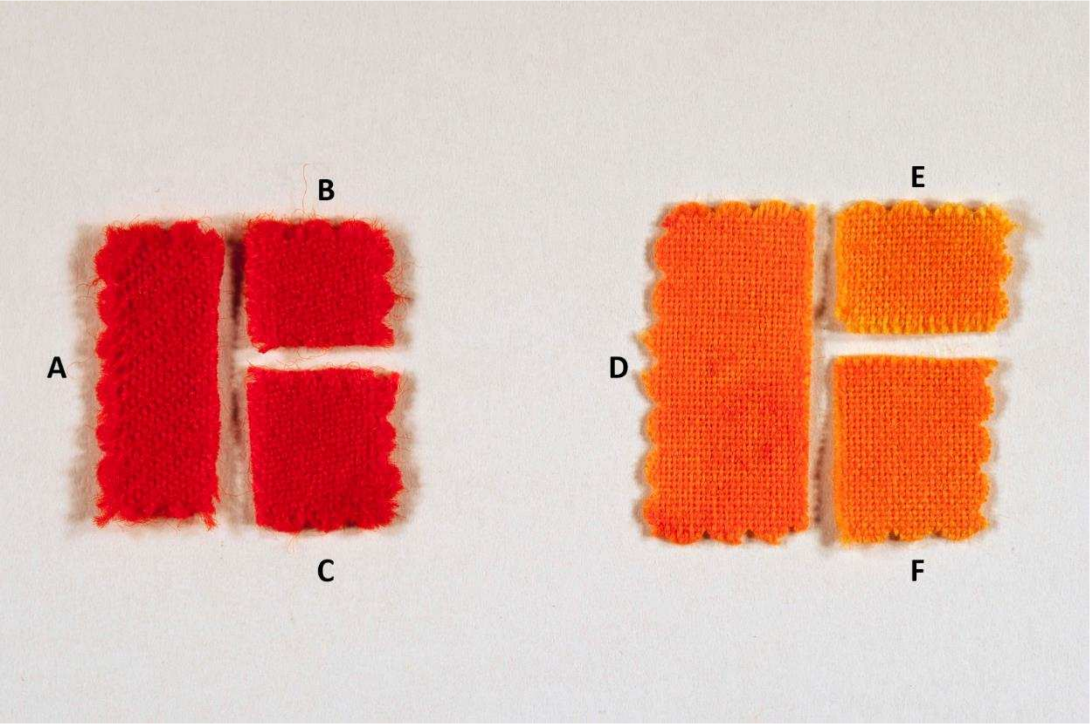


Fig. 11. Dyed wool and cotton samples using RD 1 in $scCO_2$.

The dyeing conditions were: wool - 90 °C, 140 bar, 5 % omf of dye, 40 % omf of water pre-treatment, 180 minutes dyeing time; cotton - 90 °C, 140 bar, 5 % omf of dye, 30 % omf of water pre-treatment, 180 minutes dyeing time.

It can be seen that the dyed wool sample had a stronger orange colour than the dyed cotton. It is difficult to discern the colour difference between washed (Sample B)/extracted (Sample C) wool and dyed wool (Sample A). A commercially viable level dyeing was observed on the dyed wool sample.

The dyed cotton was relatively light orange in colour. Samples faded after the wash and extraction. More colour was lost when the cotton sample was extracted using acetone and water compared to a general wash using water and detergent. The poorly dyed cotton sample had some coloured spots on the fabric.

4. Conclusion

A major benefit of using the vinyl sulphonyl reactive group is the nucleophilic addition reaction between the fabrics and the dyes, which provides the elimination of basic conditions in the dyeing system. This makes it possible to dye wool fabrics under neutral conditions, and even in mildly acidic environments, such as $scCO_2$.

In this study, a general process has been demonstrated to synthesise a reactive disperse dye containing the vinyl sulphonyl group, starting from a thiol. It is a simple method to add the vinyl sulphonyl reactive group to not only an azo dye, but also to other chromophores, such as the anthroquinone group. This has the potential to provide a wide range of hues.

Excellent dyeing results for wool were achieved with the synthesised vinyl sulphonyl modified disperse dye including colour depth, fixation and fastness. The dyeing qualities were dramatically improved by the water pre-treatment of wool fabric. The optimal dyeing conditions were 90 °C and 140 bar with 40 % omf of water remaining on the fabric after 30 minutes of water pre-treatment. The dyeing of cotton was somewhat less effective than the dyeing of wool under the stated dyeing conditions, but still had an acceptable colouration. The colour depth and fixation values were improved by using 30 % omf of water pre-treatment for cotton. Though the fixation cannot meet the commercial requirement, the colouration of the dyed cotton can still be used for other wash-free purposes, such as the dyeing of curtains. Furthermore, the results of the dyeing for both wool and cotton were comparable to traditional reactive dyes in aqueous dyeing (Lewis, 1982).

The dyeing conditions for dyeing both wool and cotton were much milder than those in the literature, indicating that there is a potential to try industrial scale experiments with this dyeing method (Abou Elmaaty and Abd El-Aziz, 2017; Bach et al., 2002; Banchero, 2013).

The synthesised vinyl sulphonyl disperse dyes are considered to be the most suitable dyes for wool and cotton fabrics dyeing in supercritical carbon dioxide. The dyeing also only requires a small quantity of water, with no other additional components required. Overall, these demonstrate that the described method is helpful for developing reactive disperse dyes containing vinyl sulphonyl functional groups. The obtained disperse reactive dye could be hopefully applied for the ecofriendly and energy-efficient supercritical dyeing of natural fabrics.

Associated content

Supporting Information: The supplementary data associated with this article contains instruments and methods information, procedure for synthesis of vinyl sulphone modified disperse azo dye and ^{1}H-NMR spectra, ^{13}C-NMR spectra, IR spectra of all the synthesised compounds. UV-Vis spectrum of the RD 1 was attached.

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Author Contributions

The manuscript was written through contributions of all authors. Mr. Richard Thompson, Mr. Jonathan White and Mr. Xujun Luo synthesised and characterised the dye successfully. Dyeing experiments were carried out with the help of Professor Christopher Rayner and Dr. Balazs Kulik. Dr. Algy Kazlauciunas helped with the analysis of the dyed fabrics. Dr. Weidong He and Professor Long Lin provided general advice on the study. All authors have given approval to the final version of the manuscript.

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