



# 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<sub>2</sub> as the dyeing medium. The optimum dyeing process was carried out with water pre-treatment at 90 °C and 140 bar during a 60 min 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.

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## 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<sub>2</sub>) to replace water as the dyeing medium. ScCO<sub>2</sub> 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<sub>c</sub> = 73.7 bar and T<sub>c</sub> = 31.1 °C).

The dyeing of synthetic fibres in scCO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub> have been proposed in the literature during the last two decades.

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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  $\text{scCO}_2$  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  $\text{scCO}_2$  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  $\text{scCO}_2$  (Sawada and Ueda, 2007).

One of the more promising concepts that could overcome the limitation of the mentioned procedures is the use of  $\text{scCO}_2$  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  $\text{scCO}_2$ . 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  $119 \text{ g m}^{-2}$ , the density of wool fabric was  $131 \text{ g m}^{-2}$ ) 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).

### 2.3. Supercritical $\text{CO}_2$ system

The Wolfson  $\text{CO}_2$  Laboratory at the University of Leeds provided the high pressure equipment that was used for the dyeing experiments in  $\text{scCO}_2$ . 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 min. An excess quantity of 3% on mass of the

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