Synthesis of Reactive Disperse Dyes for Dyeing Natural Fabrics in Supercritical CO_2

By

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The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Over the course of time, the dyeing industry has become one of the greater polluters of water worldwide. The sheer volume of water and the high concentration of additives used in textile colouration are staggering, which have already caused unrepairable damage to environment and continue to directly impact on the sustainability of textile colouration industry. "Supercritical CO_2 dyeing" uses supercritical CO_2 as the dyeing medium, enabling the reduction and even elimination of the creation of textile colouration wastewater. Supercritical carbon dioxide ($scCO_2$) has a low critical point and is non-flammable. It can be recycled, providing a promising environmentally friendly substitute for aqueous media.

Reactive disperse dyes that have both reactivity towards natural fabrics and high solubility in $scCO_2$ would offer great promise for colouring natural fabrics. In this study, the isocyanate group, as a reactive group, was introduced to disperse dyes to create reactive disperse dyes suitable for supercritical dyeing. Thus, a series of reactive disperse dyes, containing both isocyanate groups and alkyl groups were successfully synthesised. Dyeing experiments under different dyeing conditions were performed to establish the optimal dyeing conditions for these synthesised dyes.

A new synthesis route was developed to create an azo-based disperse reactive dye containing the vinyl sulphonyl reactive group, which was used to dye natural fibres using $scCO_2$ as the dyeing medium.

Using relatively moderate, optimal conditions in the $scCO_2$ dyeing processes, uniform dyeing with high colour strength and fastness properties that were similar to those from conventional aqueous dyeing were achieved on natural fabrics that were dyed with the synthesised dyes. Furthermore, there are opportunities to modify a wide range of disperse dyes following this synthesis route.

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List of Abbreviations

CO_2	Carbon dioxide
$scCO_2$	Supercritical carbon dioxide
SFD	Supercritical fluid dyeing
PET	Poly(ethylene terephthalate)
owf.	On the weight of fabric
DCM	Dichloromethane
THF	Tetrahydrofuran
SEM	Scanning electron microscopy
H-bonding	Intramolecular hydrogen bonding
DMSO	Dimethylsulphoxide
BTG	Benzoylthioglycollate
FTIR	Fourier Transform Infrared
NMR	Nuclear Magnetic Resonance
RD	Reactive Disperse
conc.	Concentrated
TMS	Tetramethylsilane
Hz	Herts

Chapter 1 General introduction

1.1 Background to the project

Most requirements of commercial cloth dyeing can be met by traditional water-based dyeing. However, water-based dyeing produces a great deal of waste water from both dyeing processes and washing processes. Moreover, drying of dyed cloth consumes a significant amount of energy. Pollution of the environment (Figure 1.1) caused by the huge volumes of effluent exiting textile-dyeing mills has made a significant contribution to the shortage of clean water on a global scale [1]. According to Long *et al.* [2], in 2010, more than 600 billion metres of fabrics were dyed, printed and finished in China, which resulted in over 24 billion tonnes of waste water being discharged to the environment, leading to a serious environmental burden even after some pre-treatments [2]. Thus, finding a new dyeing medium that can displace water is an urgent necessity.

Figure 1.1 Waste water after dyeing process [1]

It is well known that carbon dioxide (CO_2) has low critical points which were defined as the points on phase equilibrium curve. The critical pressure is approximately 73.8 bar and the critical temperature is approximately 31.1 °C [3]. The fluid state of CO_2 of which the temperature and pressure is above its critical points is called supercritical carbon dioxide (scCO_2). ScCO_2 is an excellent solvent for applications of many hydrophobic and non-polar substances under supercritical conditions [4]. In addition, CO_2 is non-flammable, non-toxic. Its recyclable properties allow it to be a promising green, safe and environmentally friendly substitute for water and other conventional solvents [5].

The application of supercritical carbon dioxide (scCO_2) was initially focused on extraction. In 1986, Sand *et al*. established and developed a method for making a thermoplastic polymer that was impregnated with components such as fragrance, pest control agents and pharmaceuticals using supercritical or near supercritical carbon dioxide or dinitrogen oxide [6]. The dyeing of textiles in scCO_2 was not invented until 1988 when Schollmeyer *et al*. established a supercritical fluid dyeing (SFD) system [7]. Apart from dyeing in pure scCO_2, some co-solvents additives such as water, alcohol and salts were also used to increase the polarity of the fluid during the dyeing process.

Further developments of SFD technology have been carried out over the last few decades. Schneider *et al.* [8] from the Ruhr-University of Bochum, Germany built the first laboratory-scale equipment for dyeing poly(ethylene terephthalate) (PET). Most attention has been given to the dyeing of PET which has many outstanding properties including that of being the most suitable textile for dyeing in scCO_2 [9-13]. PET is a semi-crystalline polymer with a glass transition temperature range of 67-81 °C. When PET is immersed in the supercritical fluid bath, the CO_2 molecules readily occupy the free space of the amorphous areas, through a plasticisation effect [14]. This phenomenon improves the diffusion of the dye molecules because the synthetic fibre becomes swollen by the CO_2 and the glass transition temperature of the fibre is reduced [15, 16].

According to Bach *et al.* [17], the most significant step in the development of the pilot plant for dyeing was the approach of Uhde GmbH in 1995. This method involved developing a total dyeing system including an extraction cycle for the removal and separation of excess dyes and spinning oils in the supercritical fluid bath. Since then, many research groups have conducted research and development in an attempt to apply the novel dyeing approach to pilot production or even mass production. Scientists from the USA, Netherlands, Germany and Italy have made great contributions to large-scale supercritical dyeing [14, 18-20]. For example, reasonably recent data on the pilot-scale dyeing of PET tested in a 24 L dyeing autoclave with a pressurised pump, a circulation pump, a heat exchangers and dye separator were reported by Huang *et al*. [21].

Figure 1.2 Commercial dyeing machine by DyeCoo [22]

The supercritical dyeing of PET has been employed for industrial production by several companies worldwide. For instance, DyeCoo Textile Systems BV has a close collaboration with world leading suppliers of athletic sportswear in production of popular sportswear range using supercritical dyeing approach. A typical industrial-scale dyeing equipment is presented in Figure 1.2. The supercritical dyeing of natural fibres such as cotton, wool and silk, however, is still very much in its infancy. The non-polar supercritical fluid, obviously, can be used to improve the dyeability of hydrophobic fibres. However, a non-polar supercritical fluid presents serious barriers to the dyeing of polar and hydrophilic fibres. Nowadays, wool and cotton as natural fibres, are widely favoured by consumers due to their comfortable service properties. Cotton has a high global market share of about 37% in the textile industry [23]. Due to the great demand for dyed wool textiles and dyed cotton textiles and the high pollution arising from the conventional aqueous dyeing processes, there is an urgent need for the creation of reactive dyes that can dissolve in $scCO_2$ that can then be covalently bonded to natural fibres, particularly wool fibres and cotton fibres.

1.2 Goals of this project

The aim of the research described in this thesis was to synthesise novel CO_2-soluble reactive dyes, so called reactive disperse dyes, for the dyeing of natural fibres. This project concerned the synthesis design, characteristics and evaluation of 5 classes of dye carrying different reactive groups. Naturally, a study of conditions optimisation for dyeing of cotton and wool with these dyes was undertaken in $scCO_2$. Thus, the synthesis of novel reactive dyes was undertaken for this purpose.

1.3 Thesis outline

Following this Introduction, chapters, these are:

Chapter 2: This chapter gives a review on different aspects of supercritical dyeing including sections on the use of carbon dioxide, colourimetry, reactive dyes, cotton and wool. These are followed by a description of the general processes, equipment used and the technological development of supercritical dyeing.

Chapter 3: This chapter deals mainly with the experimental sets-up in supercritical dyeing and in the methods of analysis including colour measurement, colour fastness and microstudy of the dyed fabrics.

Chapter 4: This chapter contains a summary, the results and discussion of dyed natural fibres. A novel reactive disperse dye was synthesised through a “simple” reaction between an azo based disperse dye and diphosgene to produce an isocyanate that contained reactive disperse dye. The synthesis has the potential to be scaled up to an industrial process. The reagents are generally inexpensive and the synthesis route presented is relatively simple.

Chapter 5: This chapter relates three highly CO_2-soluble azobenzene chromophores that were synthesised via azo coupling reactions. The isocyanate reactive group –NCO, has great affinity for cotton and for wool in the supercritical dyeing process.

Chapter 6: This chapter provides a new synthesis route to obtain a vinyl sulphone contained disperse reactive dye. The results presented relevant to dyeing involves the synthesised azo-based reactive disperse dye containing the vinyl sulphonyl reactive group, which is able to dye natural fibres under neutral conditions or even mild acidic conditions. The possibility of dyeing natural fibres using the vinyl sulphonyl unit in supercritical carbon dioxide as the dyeing medium is discussed.

Chapter 7: This chapter relates to all the characterisation of the synthesised reactive disperse dyes.

Chapter 8: Here, conclusions relating to the work carried out are covered. Suggestions for relevant future work that could be carried out, are also considered.

1.4 References

1. OEcotextiles. *Dyes – synthetic and "natural"* (online). Accessed 02/02/2017. ; Available from: https://oecotextiles.wordpress.com/2009/09/01/dyes-synthetic-and-natural/.
2. Long, J.-J., G.-D. Xiao, H.-M. Xu, L. Wang, C.-L. Cui, J. Liu, M.-Y. Yang, K. Wang, C. Chen, and Y.-M. Ren, *Dyeing of cotton fabric with a reactive disperse dye in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2012. **69**: p. 13-20.
3. Muthukumaran, P., R.B. Gupta, H.-D. Sung, J.-J. Shim, and H.-K. Bae, *Dye solubility in supercritical carbon dioxide. Effect of hydrogen bonding with cosolvents.* Korean Journal of Chemical Engineering, 1999. **16**(1): p. 111-117.
4. Brogle, H., *CO_2 Solvent: its Properties and Applications.* Chemistry and Industry, 1982. **60**(6): p. 385-390.
5. Beckman, E.J., *Supercritical and near-critical CO_2 in green chemical synthesis and processing.* The Journal of Supercritical Fluids, 2004. **28**(2): p. 121-191.
6. Sand, M.L., *Method for impregnating a thermoplastic polymer*. 1986, US 4678684 A.
7. Schollmeyer, E., D. Knittel, H.-J. Buschmann, G.M. Schneider, and K. Poulakis, *Dyeing process*, D. Textilforschungszentrum, Editor. 1990: Germany.
8. Poulakis, K., M. Spee, G. Schneider, H. Buschmann, and E. Schollmeyer, *Dyeing of polyester in supercritical carbon dioxide.* Chemiefasern/ Textilindustrie, 1991. **41**: p. 142.
9. Sicardi, S., L. Manna, and M. Banchero, *Diffusion of disperse dyes in PET films during impregnation with a supercritical fluid.* The Journal of Supercritical Fluids, 2000. **17**(2): p. 187-194.
10. Santos, W.L.F., M.F. Porto, E.C. Muniz, N.P. Povh, and A.F. Rubira, *Incorporation of disperse dye in N,N-dimethylacrylamide modified*

poly(ethylene terephthalate) fibers with supercritical CO2. The Journal of Supercritical Fluids, 2001. **19**(2): p. 177-185.

11. Fleming, O.S., S.G. Kazarian, E. Bach, and E. Schollmeyer, *Confocal Raman study of poly(ethylene terephthalate) fibres dyed in supercritical carbon dioxide: dye diffusion and polymer morphology.* Polymer, 2005. **46**(9): p. 2943-2949.
12. Ferri, A., M. Banchero, L. Manna, and S. Sicardi, *Dye uptake and partition ratio of disperse dyes between a PET yarn and supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2006. **37**(1): p. 107-114.
13. De Giorgi, M.R., E. Cadoni, D. Maricca, and A. Piras, *Dyeing polyester fibres with disperse dyes in supercritical* CO_2. Dyes and Pigments, 2000. **45**(1): p. 75-79.
14. Banchero, M., *Supercritical fluid dyeing of synthetic and natural textiles - a review.* Coloration Technology, 2013. **129**(1): p. 2-17.
15. Saus, W., D. Knittel, and E. Schollmeyer, *Dyeing of textiles in supercritical carbon dioxide.* Textile Research Journal, 1993. **63**(3): p. 135-142.
16. Nashed, G., R.P. Rutgers, and P.A. Sopade, *The plasticisation effect of glycerol and water on the gelatinisation of wheat starch.* Starch ‐ Stärke, 2003. **55**(3-4): p. 131-137.
17. Bach, E., E. Cleve, and E. Schollmeyer, *Past, present and future of supercritical fluid dyeing technology–an overview.* Review of Progress in Coloration and Related Topics, 2002. **32**(1): p. 88-102.
18. Hendrix, W.A., *Progress in Supercritical* CO_2 *Dyeing.* Journal of Industrial Textiles, 2001. **31**(1): p. 43-56.
19. Banchero, M., S. Sicardi, A. Ferri, and L. Manna, *Supercritical Dyeing of Textiles—From the Laboratory Apparatus to the Pilot Plant.* Textile Research Journal, 2008. **78**(3): p. 217-223.
20. Van der Kraan, M., F. Cid, G. Woerlee, W. Veugelers, and G. Witkamp, *Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes.* The Journal of Supercritical Fluids, 2007. **40**(3): p. 470-476.
21. Huang, G., F-.C. Dong, J-.H. Wang, and Y-.T. Jia, *Establishment of Database of Color Matching System for Supercritical* CO_2 *Dyeing.* Advanced Materials Research, 2012. **441**: p. 708-712.
22. DEXIGNER. *DyeCoo: Winner of the Third Annual MEDIUM Award for Material of the Year* (online). Accessed 02/02/2017; Available from: https://www.dexigner.com/news/25160.
23. Schmidt, A., E. Bach, and E. Schollmeyer, *The dyeing of natural fibres with reactive disperse dyes in supercritical carbon dioxide.* Dyes and Pigments, 2003. **56**(1): p. 27-35.

Chapter 2 Literature review

The literature review covers the properties of carbon dioxide, of reactive dyes, of colour, of cotton, and of wool. A summary of available dyeing equipment, the dyeing processes and the development of $scCO_2$ for use in dyeing is given to represent the potential of this technology. Understanding the essential features of the supercritical dyeing processes enables chemists to synthesise promising dyes for this environmentally friendly dyeing process.

2.1 Carbon dioxide

Carbon dioxide (CO_2) is one of the more common gases in nature, being a trace amount of gas at the concentration of around 0.04% by volume in air. CO_2 also occurs naturally in groundwater, ice caps, glaciers, rivers, lakes and seas. Over the last century, the atmospheric CO_2 concentration increased from 200 ppm to 404 ppm, as detected in December 2016 [1, 2]. This increase was mainly due to anthropogenic activities [1]. The increasing carbon dioxide emissions have been recognised as having a great impact on global warming. Therefore, it has been termed a greenhouse gas. Moreover, CO_2 is one of the sources of oxygen production by organisms and green plants via photosynthesis.

2.1.1 Chemical and physical properties of carbon dioxide

The carbon dioxide molecule consists of two electronegative oxygen atoms and an electropositive carbon atom (Figure 2.1). Due to the highly linear and symmetric structure of carbon dioxide, the molecule is very weakly polar.

CO_2 is able to form carbonic acid with water reversibly. The weak acidity of carbonic acid is due to the incomplete ionisation in aqueous solution. The low molecular energy of CO_2 means that it is a relatively stable molecule that would not be expected to react with oxidising reagents. Nevertheless, because of the electron deficiency of the carbonyl carbon, CO_2 can react with strong nucleophiles and with electron-donating reagents [3].

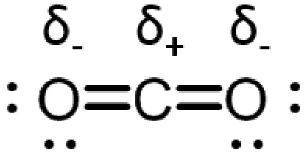


Figure 2.1 The structure of carbon dioxide

CO_2 is a colourless and odourless gas at low concentration in air. According to Figure 2.2, CO_2 gas will turn to a solid directly when the temperature fall to -78.5 °C at 1.0 atm. Solid CO_2 is termed dry ice. There is no liquid state for CO_2 at pressures below 5.2 atm. Therefore, in order to store CO_2 using the least amount of space possible, CO_2 gas is pressurised as a liquid in a high-pressure cylinder. The triple point of carbon dioxide is around 0.52 MPa at -56.6 °C. The supercritical state can be achieved at temperatures above 31.05 °C and pressures above 7.3.0 MPa. Supercritical carbon dioxide is a fluid having both gas and liquid properties, which can penetrate a solid like a gas, but also dissolve material like a liquid.

2.1.2 Applications of carbon dioxide

Carbon dioxide has been used in a wide variety of applications (Figure 2.3). For instance, in the food industry, carbon dioxide is generated by fermentation to expand bread during baking (Figure 2.3a). Sparkling drinks are produced by pressurised CO_2, such as soda water, coke etc. (Figure 2.3b). Because of the non-flammability and cheapness of carbon dioxide, it can be used in fire extinguishers (Figure 2.3c). Carbon dioxide, as a precursor to chemicals, also plays a very important role in chemical industries (Figure 2.3d).

Supercritical carbon dioxide ($scCO_2$) technology has been well established in a range of pharmaceutical and chemical processing industries for many decades. The non-toxicity, non-flammability, and low cost of $scCO_2$ makes it an environmentally acceptable solvent for various applications [10].

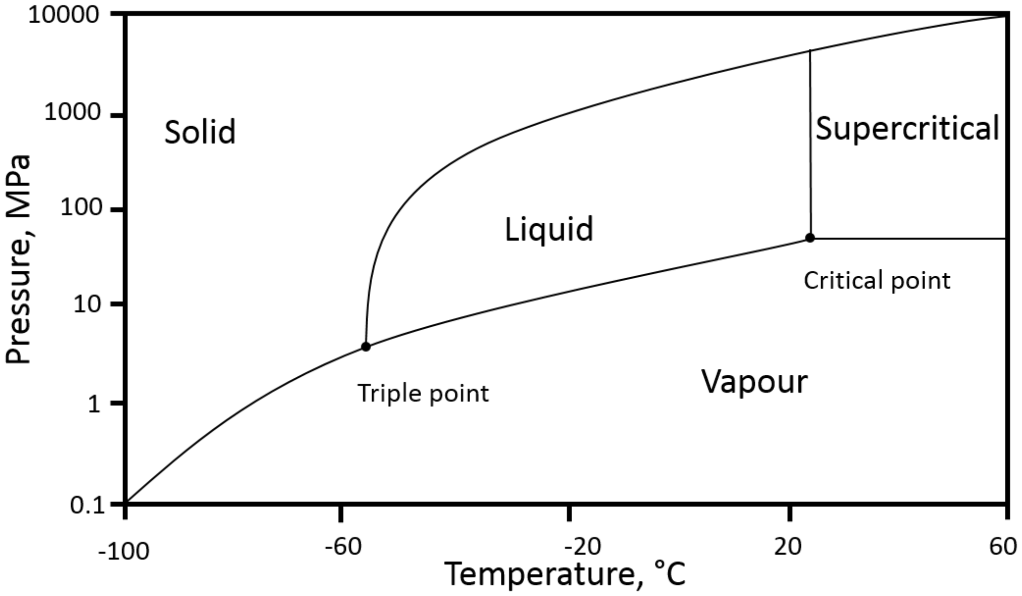


Figure 2.2 CO_2 phase diagram [4]

Besides the gas-like low viscosity and liquid-like high diffusion rate, $scCO_2$ can be an excellent alternative to many harmful and volatile organic solvents. Supercritical extraction (Figure 2.3e) is a method to extract essential oils and other herbal distillates. It occurs by changing the temperature and the pressure to control the density of $scCO_2$, which has been industrialised over the last seventeen years [11]. Scientist used $scCO_2$ to replace water in enhanced oil recovery. Two of the major advantages of using $scCO_2$ in this way are that it can reduce the viscosity of the oil when the crude oil is mixed with $scCO_2$ and it is an effective approach to obtaining crude oil [12]. With a view to saving water, supercritical dyeing (Figure 2.3f) was pioneered by Schollmeyer *et al.* and has since been developed into an extensive area of research and technology [13].

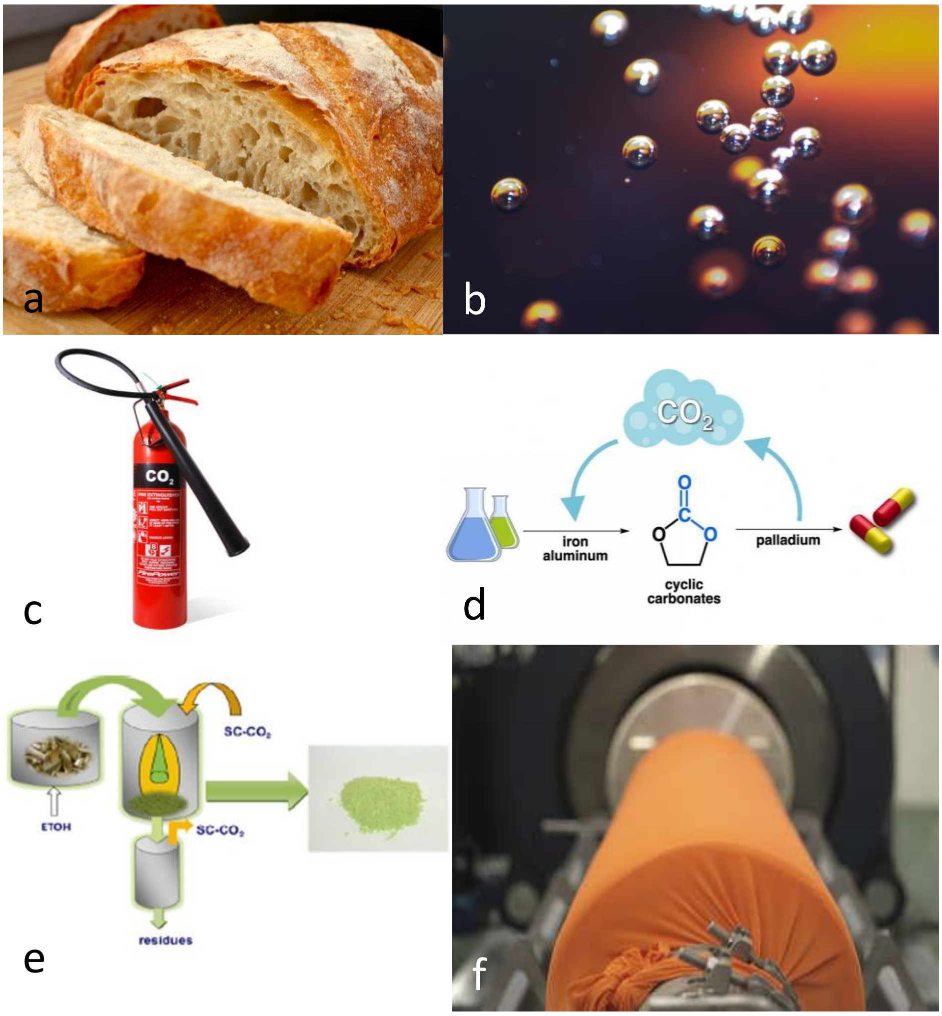


Figure 2.3 Applications of CO_2: (a) CO_2 voids generated by fermentation in a piece of bread; (b) CO_2 bubbles in a soft drink; (c) CO_2 in a fire extinguisher; (d) CO_2 when used to transform simple molecules into cyclic carbonates, which are then converted into valuable pharmaceuticals; (e) the process of supercritical extraction; (f) Supercritical dyeing of PET [5-9]

2.2 Dyes

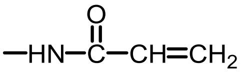
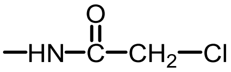
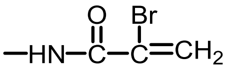
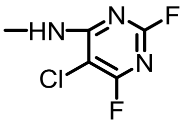
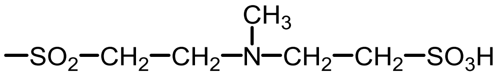
2.2.1 Traditional reactive dyes and disperse dyes

The first commercial reactive dye was invented in the early 1950's at Imperial Chemical Industries (ICI) in England. A reactive dye, which is generally a water-soluble salt, consists of a chromophore group and a reactive group that is capable of forming a covalent chemical bond with fibres. The advantage of dyeing cellulose and protein fibres with reactive dyes is that the formation of a chemical bond greatly improves the wash fastness and rub resistance.

Reactive dyes can provide good degree of wet fastness, for a full range of colourants. They have advantages in dyeing fabrics, especially natural fabrics. Natural fabrics have a large number of reactive sites that can potentially form covalent bonds with reactive dyes. Examples include the hydroxyl groups in cotton fibres, and amino, thiol and hydroxyl groups in wool. Such fabrics can reactive with conventional reactive dyes under a wide range of conditions [14].

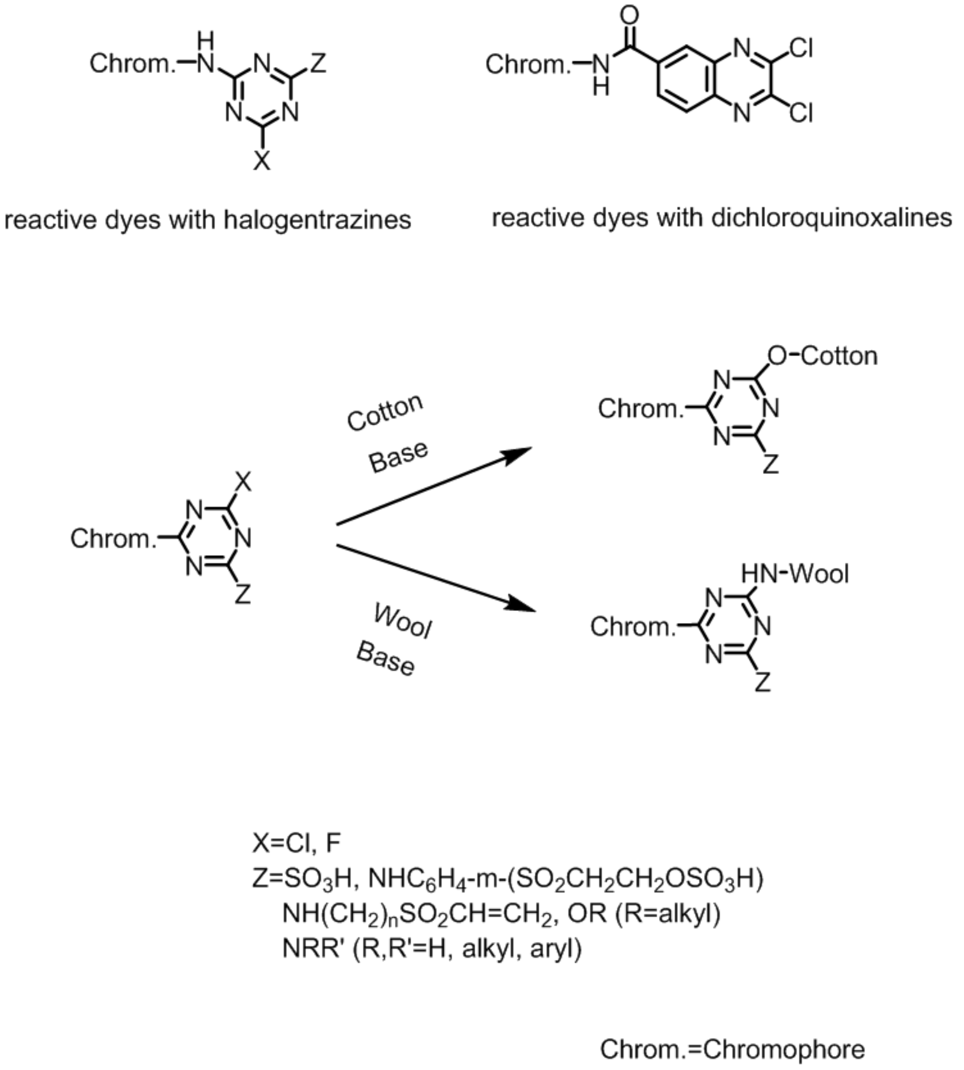
The reactive groups of the more widely commercialised reactive dyes classes for dyeing natural fibres are summarised in Table 2.1 [14]. These dyes can be divided into two groups, nucleophilic substitution reaction dyes and Michael addition reaction dyes. Their mechanisms were presented in the Section 2.2.2

Table 2.1 The most common reactive groups for reactive dyes for wool and cotton [15]

Name of the reactive group	Structure	Year of introduction
Acrylamido	 $-\mathrm{HN}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH}{=}\mathrm{CH_2}$	**1964**
ω-chloroacetyl	 $-\mathrm{HN}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{Cl}$	**1966**
α-bromoacrylamido	 $-\mathrm{HN}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{Br}}{\vert}}{\mathrm{C}}{=}\mathrm{CH_2}$	**1969**
2,4-difluoro-5-chloropyrimidyl		**1971**
N-methyltaurine-ethylsulphone	 $-\mathrm{SO_2}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\mathrm{CH_3}}{\vert}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{SO_3H}$	**1971**
β-sulphatoethylsulphone	$-\mathrm{SO_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\text{-}\mathrm{SO_3H}$	**1971**

A conventional reactive dye for cotton or wool is a water soluble compound having a reactive group that can be classified according to the three simple reaction mechanisms involved in their fixation: a) bimolecular (heteroaromatic) nucleophilic substitution, b) nucleophilic addition, and c) ester (especially phosphonate) formation [19].

Molecular structures and reaction mechanism of typical heteroaromatic reactive dyes are shown in Figure 2.4 [19]. Thus, the nucleophilic functional hydroxyl group reacts with an electron-deficient centre of the reactive group in the presence of a base to give an ether linkage. Then, the leaving group of the reactive dye will be eliminated.

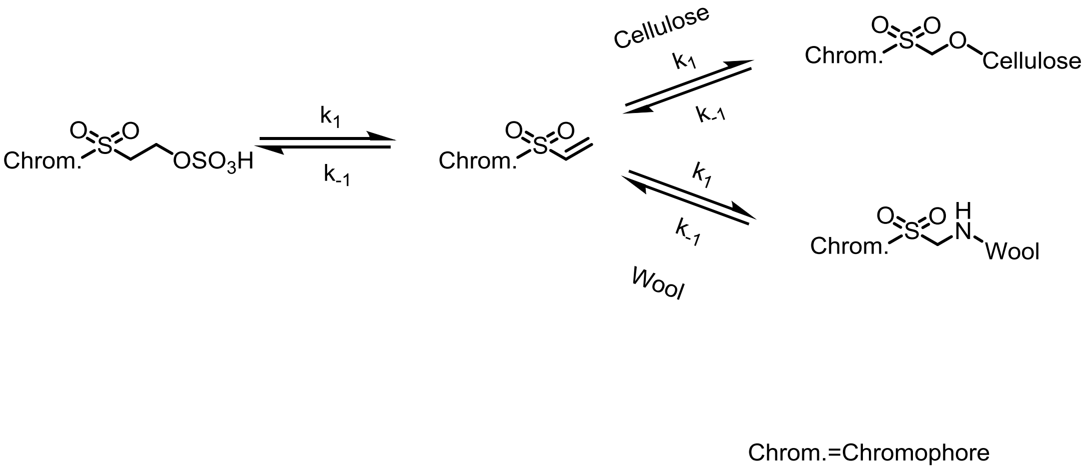


X=Cl, F
Z=SO_3H, NHC_6H_4-m-($SO_2CH_2CH_2OSO_3H$)
$NH(CH_2)_nSO_2CH=CH_2$, OR (R=alkyl)
NRR' (R,R'=H, alkyl, aryl)

Chrom.=Chromophore

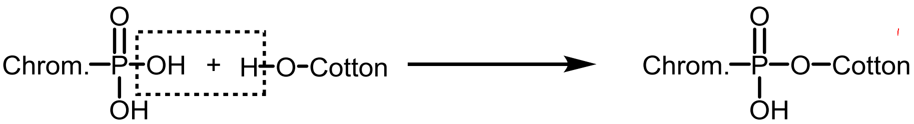
Figure 2.4 Structure of typical heteroaromatic reactive groups and their reaction with cotton fibres and wool fibres

The most significant functional group in the nucleophilic addition series is the [(sulphoxy)ethyl]sulphonyl reactive functional group which readily generates reactive vinyl sulphone intermediates under basic conditions (Scheme 2.1) [19]. Obviously, the mechanism of nucleophilic addition reaction is quite different from the nucleophilic substitution one, as the elimination step is only determined by the leaving group of dye.



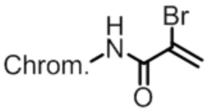
Scheme 2.1 Process of nucleophilic addition reaction

A reactive dye that has a phosphonic acid group (Scheme 2.2) can form covalent bonds to cellulose [20]. This dye, which combines a chromophore and reactive dye, was commercialised by Imperial Chemical Industries [19].

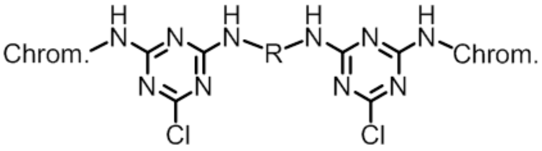


Scheme 2.2 Process of phosphonate ester reaction

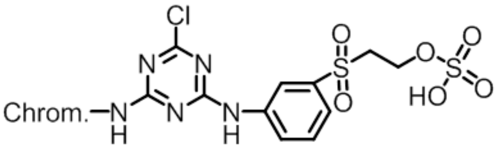
In attempts at achieving a high degree of fixation, bifunctional reactive dyes that have two identical or different reactive groups, (Figure 2.5), in a dye molecule have been synthesised [21, 22]. Although adding more reactive sites could increase the opportunities of reaction with the cotton, the colour depth per unit weight of dye decreases since the percentage of chromophore in the dye molecule is reduced [23]. Another remarkable advantage of the double-anchor reactive dyes is that they allow the dyes to operate under a wider range of dyeing temperature and fixation pH than dyes containing one group or two identical groups [23]. These merits make dyeing possible under different conditions even in the supercritical fluid system, if the suitable functional groups are selected.



Dyes with biifunctional reactive groups 2-bromoprop-2-enamido



Double-anchor reactive dyes with two equivalent reactive groups

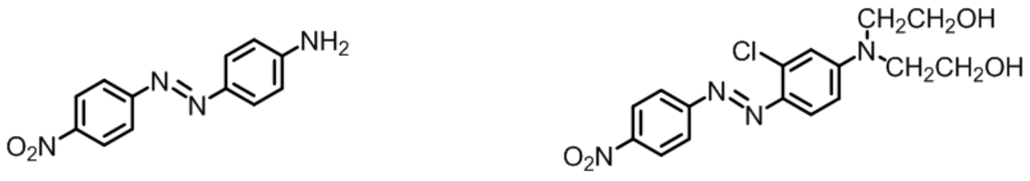


Mixed-anchor reactive dyes with two different reactive groups

Chrom.=Chromophore

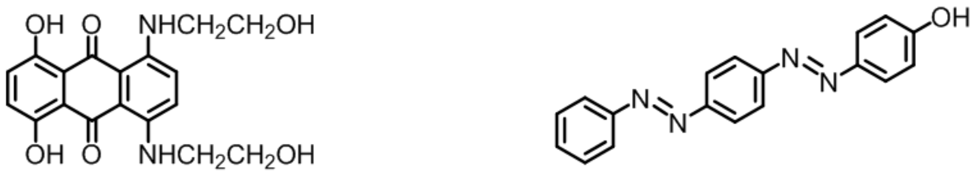
Figure 2.5 Examples of representatives of bifunctional reactive dyes having two identical reactive groups or two different reactive groups [19, 23, 24]

Disperse dyes are non-polar molecules that are based mainly on either azobenzene or anthraquinone chromophores. Some examples of disperse dye are presented in Figure 2.6. Disperse dyes are typically used as dispersions in aqueous media due to their insolubility in water. Often, dispersing agent additives are required for the dyeing process. Disperse dyes are used to dye hydrophobic synthetic fibres, such as poly(ethylene terephthalate) (PET) or cellulose acetate with reasonable colour and wash fastness [16].



C.I Disperse Orange 3

C.I Disperse Red 7



C.I Disperse Blue 7

C.I Disperse Yellow 23

Figure 2.6 Examples of commercialised disperse dyes

2.2.2 Structure of reactive disperse dyes

Contrary to conventional dyeing, traditional reactive dyes cannot be dissolved in $scCO_2$ in supercritical dyeing. Some of the non-polar, water-insoluble disperse dyes that are used in the dyeing of non-polar, hydrophobic polyester in supercritical fluid, are soluble in $scCO_2$, but they have no affinity to polar natural fabrics [17].

To overcome these limitations, attempts to dye natural fibres with the so-called reactive disperse dyes that combine the properties of solubility in $scCO_2$ and their high reactivity towards natural fibres has been made with some success [18].

As previously mentioned, compared with the traditional reactive dyes and disperse dyes, those chosen to dye cotton in $scCO_2$ should be CO_2-soluble and highly reactive. Therefore, the non-polar chromophoric part that is soluble in CO_2 should have two groups: the chromophore group and the CO_2-solubilising group(s). . Several disperse dyes that have been modified with reactive groups are represented in the Figure **2.7**.

The dyes presented in the Figure **2.7** are: a: C.I. Disperse Yellow 23 modified with 2-bromoacrylic acid; b: N-(4,6-dichloro-1,3,5-triazine-2-yl)-N-{5-(diethylamino)-2-[(4-nitrophenyl)diazenyl]phenyl} amine; c: Fluorotriazine/ chlorotriazine modified azo dyes; d: Halogenated acetamide azo dyes e: Bi-acyl fluoride modified azo dye; f: N, N-diethyl-4-[(E)-(4-vinylsulfone)phenyl)azo] aniline; g: C.I. Disperse Yellow 23 modified with 1,3,5- trichloro-2,4,6-triazine.

Some reactive disperse dyes have demonstrated to have good dyeing ability for natural fabrics in $scCO_2$ with organic co-solvent, such as methanol [2]. However, none of these achieves both great colouration of fabrics and good fastness qualities (e.g. water, light and rub fastness) without any additives in $scCO_2$ or pre-treatment of cotton and wool. One of the more important reasons is that most of the reactive groups need to react chemically with the fabric under basic condition; however, the reactivity of the reactive groups is not great in the mild acidic $scCO_2$ environment.

Overall, the synthesis of novel reactive dyes need the dyes to meet four requirements: to be non-toxic, to be CO_2-soluble, to have affinities for natural fibres and to have a high reactivity in $scCO_2$.

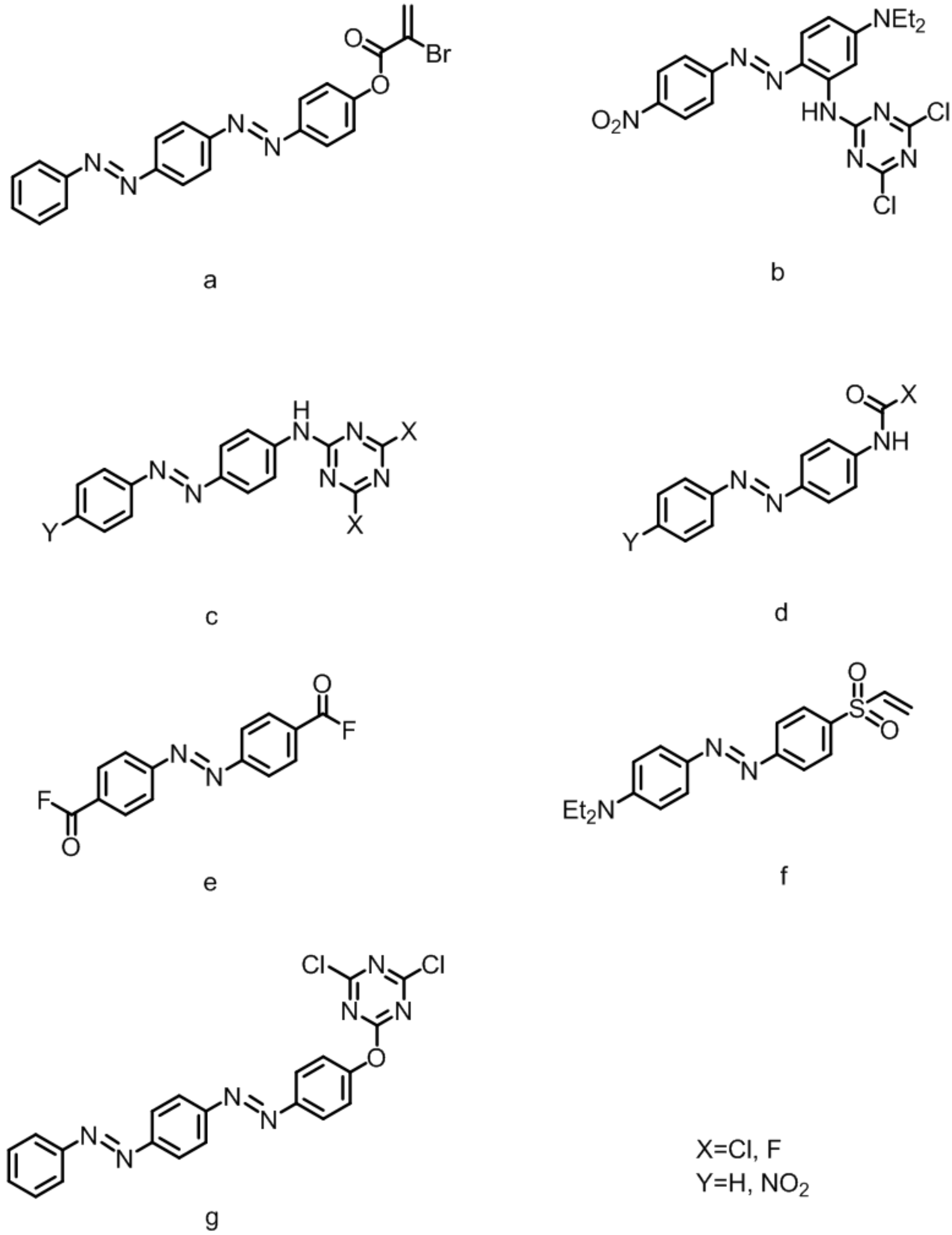


Figure 2.7 Previously disclosed reactive disperse dyes [18, 25-29]

2.2.3   Solubility of disperse dyes in scCO$_2$ and of reactive dyes in scCO$_2$

Besides the major factor of structure and reactivity/interactivity, the solubility of disperse dyes can be improved in supercritical fluid by altering the effective density of the fluid by varying pressure and temperature [30, 31]. Many publications have recorded solubility data of more than 90 dyes in $scCO_2$ since the 1990s. Half of these were published recently [32]. According to the aforementioned data, generally the solubility of disperse dyes is low in $scCO_2$, being similar to water [33-35], over a wide range of temperatures and pressures.

Many trials were conducted to establish a connection between the solubility of the dyes in $scCO_2$ and other properties of the dyes [36-38]. However, there was no convincing evidence to explain their correlation [37]. If highly polar groups such as hydroxyethyl, amino, cyano, acetylamino and carboxy groups are introduced into disperse dyes, the solubility is very low [30, 31, 37]. Moreover, dyeing in a static supercritical fluid without circulation, molecules readily aggregated to form associates and crystals, which apparently decreased the solubility in $scCO_2$ [39]. High molecular weights and intra hydrogen bonding within and between the dyes also resulted in low solubility [37].

It has been demonstrated that it was possible to improve the solubility of disperse dyes under supercritical conditions by chemical methods and by physical methods. Those non-polar disperse dyes that are based on azo groups and/or anthraquinone groups modified with halogen and nitro groups that seem to have a positive effect on solubility, are readily soluble in the non-polar $scCO_2$ [37, 40-43]. Intramolecular hydrogen bonding (H-bonding) weakens the interaction between dye molecules, consequently increases solubility [27, 34, 44]. Furthermore, a small amount of a modifier, such as water, acetone, alcohols or dimethylsulphoxide (DMSO) added to compressed carbon dioxide has proven to improve the solubility of solutes successfully. This behaviour can be explained by the increases in solvent density, in polarity and in the formation of hydrogen bonds between the co-solvent and the dyestuff [45, 46].

Theoretically, greater solubility would be obtained if the dyeing was carried out in a circulated supercritical fluid with extensively ground disperse dyes, increasing the surface area of the dyes [30]. Density-based dyes are affected by pressure, which was determined by a large body of research. The most common correlation between pressure and solubility in $scCO_2$ is that as pressure increases, solubility increases due to the increasing density of the supercritical fluid [36, 47, 48].

Findings show that there is no clear trend of the effect of temperature. Some disperse dyes demonstrated that they were consistently soluble at higher temperatures, corresponding to that of water. However, there were some other publications indicating that solubility of some disperse dyes increases with decreasing temperature at constant pressure [37, 39, 49-51]. This is likely attributed to a significant decrease of the density and/or much lower polarity and some uncertain factors at high temperatures in $scCO_2$ [49].

Only one solubility study has been published for a reactive disperse dye [49], even though it is regarded as the most promising dye for dyeing cotton in $scCO_2$ [18]. In this paper, C.I. Disperse Red 17 was used as the disperse group that was esterified with a derivative of 1,3,5-trichloro-2,4,6-triazine (Figure 2.8). The resulting solubility was very low (mole fraction: 10^{-6}).

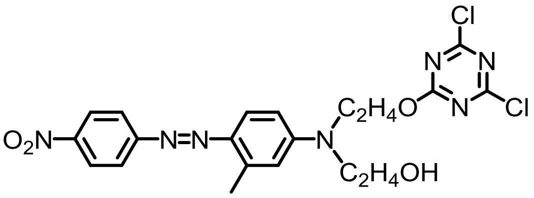


Figure 2.8 Structure of the C.I. Disperse Red 17 modified with 1,3,5-trichloro-2,4,6-triazine

The solubilities of dyes can be correlated by using an equation of state, such as the Peng-Robinson equation of state, the Redlich-Kwong equation of state and the Soave-Redlich-Kwong equation of state, and by employing an expanded liquid model that considers the supercritical fluid as a liquid phase [2], which can be represented by empirical values. It is noteworthy that the best correlation among these model is given by the Chrastil model, which has been tested several times [2, 52, 53]. Quantitative structure-property-relationship modelling (QSPR) and neutral networks methods have been used to give predictions for their supercritical fluids [2, 54], This gives a direction for the synthetic design and selection of novel dyes with proper functional group that are soluble in $scCO_2$ [2].

2.2.4 Dye partition equilibrium between fibres and $scCO_2$

The equilibrium of dye partitioning between the fibres and the fluid, like that of solubility, depends mainly on the temperature, the pressure, the dyeing time and the concentration of dye, which are some of the more influential factors of the supercritical dyeing process [55-57]. Generally, the equilibrium partition coefficient (K_{eq}) defined by the adsorption rate constant (k_a) over desorption rate (k_d) constant, (Equation 2.1), is the major guide to equilibrium partition [58].

$$K_{eq} = k_a / k_d$$

Equation 2.1 Equilibrium partition coefficient

While equilibrium data relating to dye partitioning between $scCO_2$ and PET, which have successfully been applied in supercritical dyeing, have been published [2, 55, 59], few groups have investigated the equilibrium of dye uptake in natural fibres. This is mainly due to the fact that currently no dye is well suitable for dyeing cellulose fibre or protein fibre. However, the research results of distribution of dye between $scCO_2$ and PET are of certain reference value for that of natural fabrics.

Ferri *et al.* [59] stated that according to the exothermic data in their work, a simple trend could be observed in that the partition coefficients of disperse dyes decreased with an increase in pressure because the dyes more readily dissolved in the supercritical fluid when the pressure was increased, at a constant temperature. On the other hand, the influence of the temperature on the equilibrium process is more complex. Some researchers [2, 33] have shown that the partition coefficient was increased if the temperature increased at a constant pressure, while others [58] indicated the opposing result. Further studies show that the partition coefficient decreases with an increase in temperature under constant density conditions [59]. Increasing both the pressure and the temperature leads to a greater concentration of the dye in the supercritical fluid because of the increased density. Under these conditions, both the rates of desorption and of adsorption, on PET, increase with the increasing rate of desorption increasing to a larger extent. Thus, the partition coefficient decreases in value [2].

Even though the addition of a co-solvent contributes significantly to achieving a greater concentration of the dye in PET, a decrease of the dye uptake in the synthetic fibre can be observed [60]. The root cause of this phenomenon is that the dye solubility improvement in the $scCO_2$ is much higher than the dye absorption in $scCO_2$ and the swelling of the PET [61].

For synthetic fabrics, to make the dyeing process more efficient, working under conditions in which K_{eq} is maximal is preferable. This results in obtaining the highest degree of exhaustion [30]. In other words, dyes with high solubility in the supercritical fluid have a low K_{eq}, a low colour yield being the result [30, 58].

It would be a slightly different situation if reactive dyes were applied for dyeing of natural fabrics. Great solubility of dye commonly means a weaker polar molecular structure the dye has, leading to less affinity to the relatively polar natural fabrics. Moreover, once the covalent bonds were formed between dyes and fibres, the dyes would not transfer back to the $scCO_2$. Thus, the dye partitioning between $scCO_2$ and fabrics would not only be related to temperature, pressure and solvent, but also to the reactivity of the dye.

2.3 Colourimetry

2.3.1 Nature of colour

There are many different categories of electromagnetic waves (Figure 2.9), such as ultraviolet rays, infrared rays, γ-rays and X-rays etc. What is termed the visible spectrum, is the band ranging a wavelength from 380 nm to 770 nm. Visible light can be divided into three parts: short wavelength, medium wavelength and long wavelength corresponding to the so-called primary colours: blue, green and red [62].

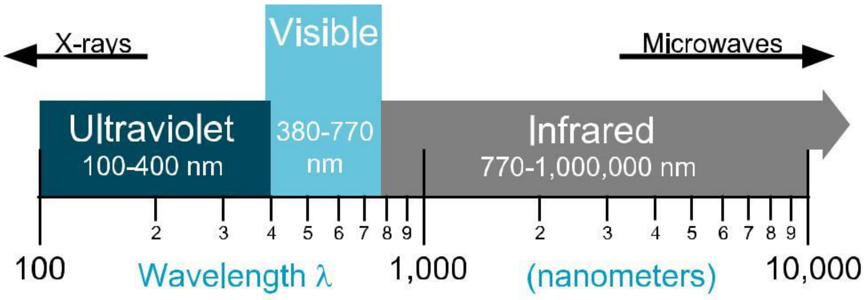


Figure 2.9 The optical portion of the electromagnetic spectrum [62]

2.3.2 CIE system

2.3.2.1 CIE XYZ colour space

In practice, it would be difficult to define a colour by human perception. Thus, in order to describe a colour, in 1931, the International Commission on Illumination (CIE) established the CIE 1931 XYZ colour space based on measurements of human colour perception. In this colour space, X, Y and Z correspond to red, green and blue.

A standard (colourimetric) observer was created in order to eliminate the variation of results from different instruments. The CIE 1931 Standard Colourimetric Observer is also known as the CIE 1931 2° Standard Colourimetric Observer. In 1964, CIE defined a 10° Standard Colourimetric Observer suggested to be used for more than about a 4° field of view.

2.3.2.2 CIE $L^*u^*v^*$ colour space and CIE $L^*a^*b^*$ colour space

Two more widely used models were introduced to improve the visual uniformity. One is CIE $L^*u^*v^*$ colour space, updated as a nearly uniform chromatic space by International Commission on Illumination in 1976. This system was designed for self illuminant’s colour space, due to its linear addition properties [64]. The two coordinates u^* and v^* were defined as follows Equation 2.2:

$$L^* = \begin{cases} \dfrac{\left(\frac{29}{3}\right)^3 Y}{Y_n}, & \dfrac{Y}{Y_n} \leq \left(\dfrac{6}{29}\right)^3 \\ 116\left(\dfrac{Y}{Y_n}\right)^{\frac{1}{3}} - 16, & \dfrac{Y}{Y_n} > \left(\dfrac{6}{29}\right)^3 \end{cases}$$

$$u^* = 13L^*(u' - u'_n)$$

$$v^* = 13L^*(u' - u'_n)$$

$$u' = \frac{4X}{X + 15Y + 3Z} = \frac{4X}{-2x + 12y + 3}$$

$$v' = \frac{9Y}{X + 15Y + 3Z} = \frac{9y}{-2x + 12y + 3}$$

Equation 2.2

Here L^* is the CIE 1976 lightness, Y_n and u'_n are values for a reference white for the illumination. X, Y and Z are tri-stimuli values of the measuring samples.

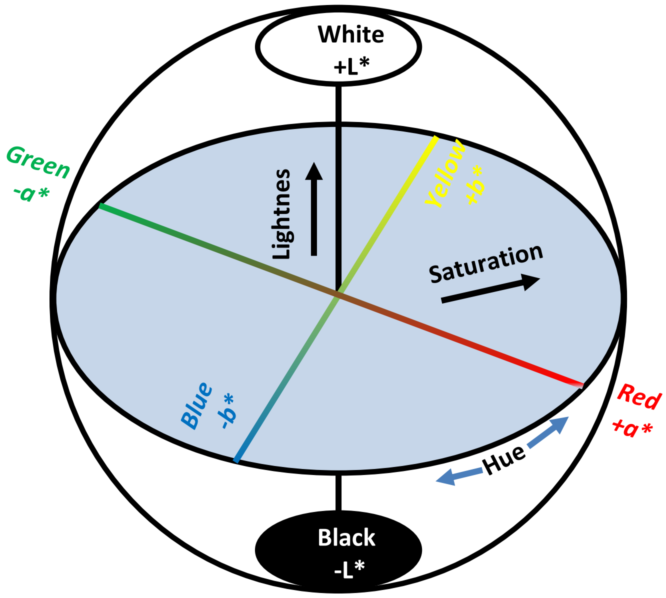


Figure 2.10 CIE L*a*b* 1976 colour space

The other commonly used model was called the CIE L*a*b* colour space, a non-self illuminant's colour space that was used in the current research to detect the colour of the surface of dyed textiles. Most models of perceived colour contain three components: lightness, hue and saturation. In the CIE $L^*a^*b^*$ model, the colour differences perceived by humans correspond to distances when measured colourimetrically. In this model, colour is modelled as a sphere, (Figure 2.10), with lightness (L) comprising the linear transform from white to black and hues modelled as opposing pairs, with saturation being the distance from the lightness axis. The 'a' axis extends from green (-a) to red (+a) and the 'b' axis from blue (-b) to yellow (+b) [62].

The equation of the CIE $L^*a^*b^*$ colour space is given in Equation 2.3:

$$L^* = 116f\left(\frac{Y}{Y_n}\right) - 16$$

$$a^* = 500\left(f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right)$$

$$b^* = 200\left(f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right)$$

Equation 2.3

$$\text{where } f(t) = \begin{cases} \sqrt[3]{t} \\ \frac{t}{3\delta^2} + \frac{4}{29} \end{cases}$$

$$\text{if } t > \delta^3 \text{ otherwise}$$

$$\delta = \frac{6}{29}$$

X_n, Y_n and Z_n are values for a reference white for the illumination. X, Y and Z are tri-stimuli values of the measuring samples.

2.4 Dyeing cotton fabric in $scCO_2$

2.4.1 Structure of cotton

Cotton is a polysaccharide structured natural product, mainly constructed by repeating anhydro glucose units connected together through covalent bonding. Table 2.2 gives the components of a typical cotton.

Table 2.2 Composition of a typical cotton [65]

Constituent	Proportion of dry weight (%)
Cellulose	94.0
Protein	1.3
Pectin	1.2
Wax	0.6
Ash	1.2
Other substances	1.7

Cellulose is essentially a condensation polymer of β-(D)-glucopyranose containing 1,4-glycosidic bonds. The degree of polymerisation of cellulose varies from 50000 to 2500000 with its source [65]. A repeating cellulosic unit of cotton is shown in Figure 2.11. The repeating unit has one primary alcohol group and two secondary alcohol groups that are chemically reactive in dyeing process. Usually, when the esterification occurred under basic condition, the reactivity will be in the order: C(2)OH > C(3)OH > C(6)OH (C represents carbon atoms. e.g. C(2) is the number 2 carbon in cellulose, see Figure 2.11). On the other hand, when the esterification occurred in an acidic environment, the reactivity order will be changed: C(6)OH > C(3)OH > C(2)OH [66]. The reaction taking place between alcohol groups in cotton and reactive dyes without breakdown of the chain may have an effect only on small area, such as, terminal groups changing [66].

The cotton polymer structure consists of ordered groups (crystalline area) and disordered regions (amorphous area). The dye molecules may mainly interact with the disordered segments (around 30 % of polymer backbone) [67]. In order to obtain better dyeing results, the swelling of cotton is a critical step in dyeing process to increase the amorphous area of the cotton and break down the intermolecular hydrogen bonds in cotton. Therefore, swelling of the fibres is advantageous to the dyeing process, as the reactive sites become more accessible to the dyes due to the crystallinity of the fibres becoming more disrupted.

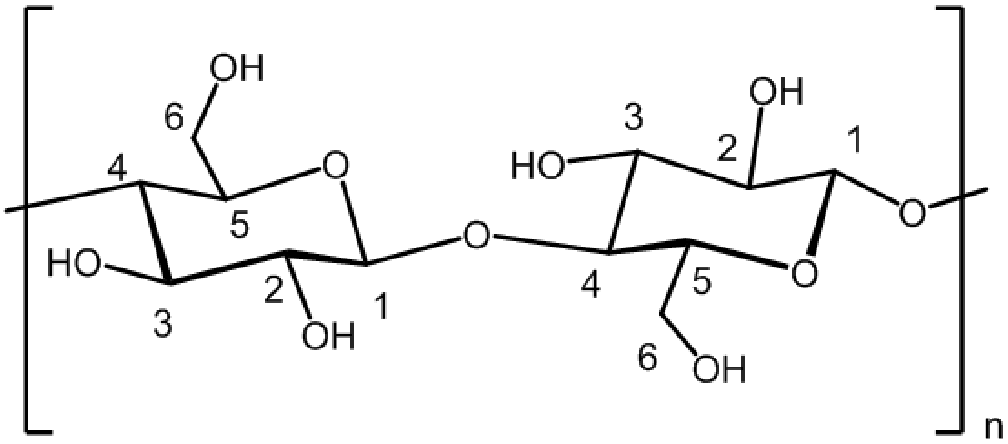


Figure 2.11 The cellobiose repeating cellulose unit found in the structure of cotton cellulose

2.4.2 Interactions between $scCO_2$ and textiles

The effects of supercritical carbon dioxide on textile polymer fibres is an essential research theme for dyeing processes since the impregnation of supercritical fluid results in hugely different properties and characteristic changes to fibres that may affect the quality of the final product [30, 68].

Many reports have covered the interaction between $scCO_2$ and PET since PET is an outstanding synthetic fibre that occupies a large textile market share, offering advantages in this dyeing medium [48, 69, 70].

The plasticisation effect of $scCO_2$ on PET is a phenomenon that can improve the mobility of the polymer chain and increase the migration of spaces into PET [30]. Wide-angle X-ray scattering (WAXS) measurements have been used in the analysis of different PET types, demonstrating that an increase in crystallinity occurs after the impregnation in $scCO_2$. For crystalline polymers, however, only a slight increase in the dimensions and the order of the crystallinity occurs[30, 71].

Morphological changes can lead to changes in the thermo-mechanical behaviour that can change the glass transition temperature (T_g) [72]. With amorphous polymers, the greater the percentage of the disordered regions, the more $scCO_2$ can be absorbed in the free volume of the polymer (swelling) and the greater is the reduction in T_g [30]. Such a decrease in the glass transition temperature allows the dyeing process to be conducted under lower temperature conditions allowing for energy savings and for an enhancement of dyeability of the substrate.

Natural polymers such as cotton, are relatively highly ordered. They do not change significantly in $scCO_2$. Thus, the inability of the non-polar and hydrophobic $scCO_2$ to swell the polar cotton fabric is one of the bigger challenges [30]. For cotton, according to conventional dyeing theory, dyes can only absorb and diffuse in the free volume in disordered areas after being impregnated by and plasticised by water. Moreover, intramolecular hydrogen bonding in cotton is an obvious hindrance to the diffusion of dyes into the fibre. In $scCO_{2,}$ cotton will become dehydrated, reducing any inherent accessibility. The dehydration of cotton in $scCO_2$ would lead to higher degree of crystallinity and orientation of the cotton. All of these factors would reduce the dye uptake rate. According to Schmidt *et al.* [73], it is possible to conduct the dyeing process for cotton under 160 °C without shrinkage or damage to the fibre.

2.4.3 Pre-treatment of cotton & co-solvent

There were two major reported solutions to these aforementioned problems to the dyeing of natural fibres in $scCO_2$. The use of some reagents and, a viable method of physical pre-treatment are the most popular routes to overcoming the disadvantages of dyeing cotton in $scCO_2$ [2, 74, 75]. Another possibility is the chemical modification of the natural fibres by introducing a reactive group on suitable group, which can improve the affinity and interaction between textile and dyes, especially the disperse dyes [2, 76, 77]. However, the product would no longer be the natural fibre itself in a strict sense.

The addition of a co-solvent to the $scCO_2$ is another route to improve diffusion. However, greater fixation or colour depths of cotton in the $scCO_2$ cannot be guaranteed. Some protic solvents that can be used as either pre-treatment solvents or as co-solvents. Examples include ethylene glycol, tetraethylene glycol dimethylether, isopropanol, water and certain alcohols. These solvents are used to increase the polarity of the non-polar fluid, increase the mobility of cellulose chains and consequently, increase the swelling and the potential dye uptake of the cellulose fibres, as well as enhance the solubility of dyes [2, 25, 30, 78, 79]. Fernandes *at el*. [78, 80, 81] showed that methanol was the best reagent of a range, both as a pre-treatment chemical and as a co-solvent, to improve the dye adsorption and dye fixation. Although, theoretically, methanol might compete with the hydroxyl groups in the cellulose to generate side reactions to some extent, the hydrolysis of the dyes by methanol does not interfere with the reaction between cotton and the dyes [80]. However, methanol is not an appropriate additive in this context due to its volatility and toxicity. Also, dye adsorption can be enhanced greatly by adding dimethylsulphoxide (DMSO) to aprotic co-solvents [78]. The fixation of adsorbed dye is very low, because of the complexation of DMSO with the hydroxyl function groups of cellulose. These block the reactive sites of the dye and cotton [27]. In addition, there exists a big problem of removal of all these chemical pre-treatment solvents.

As far as the chemical treatment of cotton is concerned, there are two possibilities that have been developed. One is that cotton is modified with reactive groups that can be a bridge, connecting the disperse dyes to the cotton. Schmidt *et al*. [17] introduced 1,3,5-trichloro-2,4,6-triazine to cotton as a reactive linkage (Figure 2.12) that is able to react with disperse dyes containing at least one hydroxyl group or amino group. The results showed that this cotton derivative with its reactive groups gave a possible approach to dyeing cotton in scCO$_2$. Schrell *et al*. [82] patented a modified cotton treated with reactive compounds containing alkylamino groups, dyed with a disperse dye readily able to connect to the amino groups. This strategy “converts” the hydroxyl groups of cotton to the amino groups that can be substituted by chlorine atoms or fluorine atoms of disperse dyes in a moderately acidic medium.

Another possible chemical treatment is the modification of cellulosic fibres to make the fibre relatively hydrophobic. Liu *et al*. [76, 77] treated ramie fibres (cellulosic fibres) with benzyl chloride and benzoyl chloride to improve the affinity and interaction between the disperse dyes and the ramie fibres. Özcan *et al*. [83] modified cotton with benzyl chloride and sodium benzoylthioglycollate respectively before the supercritical dyeing process. Unlike the former chemical modification strategies, this did not form any covalent bond between fibres and disperse dye.

Thus, the colourant on the dyed product would be easily rinsed off by organic solvents, such as acetone. Even though there was a great improvement of the colour yield and wash fastness than that obtained without any pre-treatment, the chemical reaction alters the structure and properties of the fibres leading to poor handle [17, 25, 84] and reduced tensile properties [2, 76]. The product cannot meet current commercial requirements.

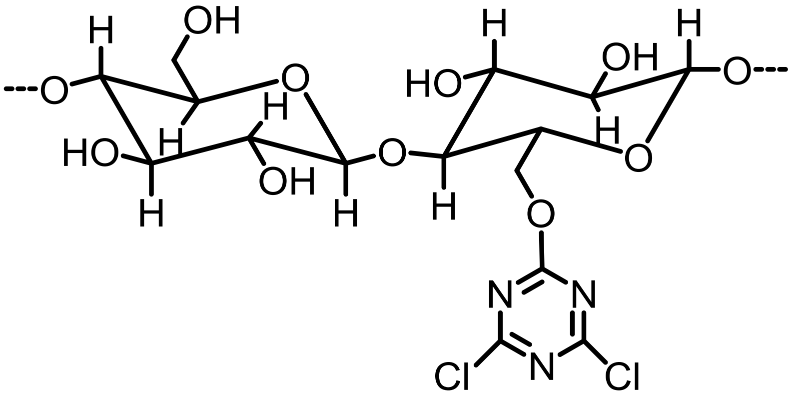


Figure 2.12 Cotton modified with 1,3,5-trichloro-2,4,6-triazine reactive groups

2.4.4 Technologies of dyeing cotton in $scCO_2$

In the last two decades, supercritical dyeing of cotton has attracted extensive attention globally after the development of new techniques that gave dyeing of PET successfully. However, the incompatibility of cotton with supercritical fluid etc. has meant that conventional dyes have extremely low affinity to cotton fibres unless pre-treatment is used [2, 26].

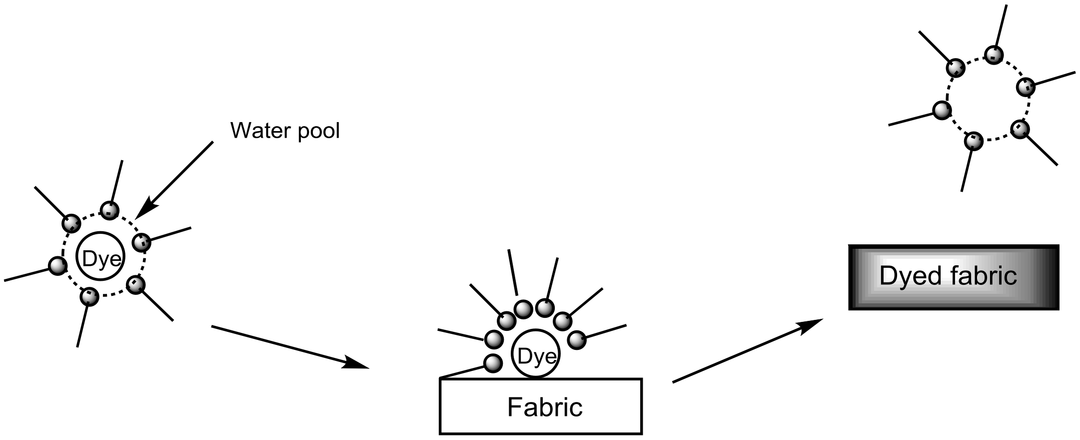
Many attempts have been made by researchers to overcome the obstacles of dyeing cotton with disperse dyes. It is possible to dye cotton fibres with reactive disperse dye (a disperse dye modified with reactive groups) in $scCO_2$ without any pre-treatment of the fibre either physically or chemically, as claimed by Schmidt *et al.* [18]. The use of reactive disperse dyes was regarded as a promising method for the dyeing of cotton in a supercritical fluid. Schmidt *et al.* [18] reported the dyeing of cotton cellulose with a disperse dye, C.I. Disperse Yellow 23 that was modified with 2-bromoacrylic acid and with 1,3,5-trichloro-2,4,6-triazine. Good wash fastness, rub fastness and light fastness (between 4 and 5) were obtained with these two reactive disperse dyes. Weak colour depths (highest K/S value of 4.83, at 280 bar and 160 °C for 240 min) was achieved after 2-bromoacrylic acid modification [18]. Acceptable results were observed. However, the low fixation value, undesirable reactive group (the low affinity to cotton under neutral condition) and the considerable thermal damage to the cotton fabrics were big hurdle for the process of additive-free dyeing in $scCO_2$ to overcome, thus hindering its success. The results obtained with no treatment on cotton, need to be improved dramatically. Many challenges exist that have not been solved.

One approach to resolving the problems is to modify chemically the hydrophilicity of cotton. One attempt at modifying cotton was reported by Saus *et al.* in 1993 [85]. These researchers used cyclohexylcarbodiimide as the modifier, making the cotton more hydrophobic, in an attempt to increase the affinity of the cotton to disperse dyes and to enhance the swellability in $scCO_2$. In 1998, Öczan *et al.* [26] demonstrated that benzoyl chloride modified cotton and sodium benzoylthioglycollate (BTG) modification of cotton could be used to improve the dyeing effects with disperse dyes APAN [1-(4-aminophenylazo)-2-naphthol] and DY82 (CI Disperse Yellow 82) in $scCO_2$. A great colour depth and a good wash fastness were achieved with benzoyl chloride modified cotton. The drawbacks were that the chlorinating reagent was toxic. Also, ring dyeing was observed due to the changes in the polarity of the fibre resulting in part penetration of the cotton by the water repelling reagent [26]. The results of the BTG modification of cotton cellulose were not as good as those obtained with cyclohexylcarbodiimide as the degree of arylation was low [26].

Schmidt *et al.* [17] patented a method of modifying cotton with the reactive group, 2,4,6-trichloro-1,3,5-triazine. They then dyed the modified cotton with disperse dyes containing hydroxyl groups or amino groups, in water or in acetone. The dyeing results demonstrated that the concentration of the reactive groups remarkably influenced its fixation values in aqueous substrates. Adding the anionic surfactant sodium dodecylsulphate resulted in a good levelness of dyeing that can be obtained at a low degree of fixation of the fibre reactive group on cotton of 3 % owf. (on weight of fibre) [17]. The dyeing results given by the modified cotton in acetone showed low fixation values at any concentration, as well as higher colour depths and poorer wash fastness [17].

Researchers have investigated how physical pre-treatments affect the dyeing results. Beltrame *et al.* [75] found that the dye uptake ($K/S = 4.2$) and fastness (3-4) were increased significantly with 8 wt. % poly(ethylene glycol) (PEG) pre-treated cotton and benzamide treated dyes. Maeda *et al.* [86] employed both tetraethylene glycol dimethylether and N-methy-1-2-pyrrolidinone to modify cotton and then dyed the modified cotton with reactive disperse dyes, in the presence of a co-solvent, acetone, which helped to improve the colour yield. They declared that over 80 % of the dye was still fixed on the cotton fibres after the washing step [86]. Fernandez Cid *et al.* [27, 78, 81], from 2003 to 2007, synthesised a series of non-polar reactive disperse dyes with fluorotriazine reactive groups that showed superior dyeing ability [27]. Methanol was the best pre-treatment reagent, as well as co-solvent. They obtained increased K/S values up to 20.2 on cotton, after being subjected to a Shoxlet extraction at 85 °C, for 1 h [27, 78]. More importantly, good fixation of almost 100% and K/S values up to 17.3 (after extraction) on methanol pre-treated cotton fibres, dyed in $scCO_2$, were obtained utilising monofluorotriazine reactive dyes by adding the co-solvent and a small amount of acid, *i.e.* H_3PO_4 and HAc (0.1, 0.3 and 0.7 % owf.) [81]. These outstanding results were reproduced on a larger scale [81]. Thus, the dyeing effects can be improved by pre-treating cotton and adding co-solvent. However, the additives increase costs and create downstream problems. Organic solvents are undesirable reagents for use in the textile industry because of their volatility and toxicity.

Sawada *et al.* [87, 88] developed a reverse micellar system of dyeing in $scCO_2$ as a new dyeing medium that can transfer water-soluble dyes, such as reactive dyes and acid dyes, to cotton fibres. The mechanism of this new water pool medium formed stably with the aid of a surfactant, pentaethylene glycol n-octyl ether, described in this report is shown in Scheme 2.3 [87]. Unsatisfactory results were obtained due to the electrostatic repulsion between the dye and the surface of the cotton, but an expected improvement was achieved by a cationic modification of the cotton fibres [87]. The dye uptake did not change with different pressures, as the solubility of dyes depend on density of water not that of the supercritical fluid [87].



Scheme 2.3 The water pool dyeing mechanism

Long *et al.* [25] took advantage of a phase transfer catalyst, triethylene diamine (TEDA) to improve the fixation on cellulose, which occurred in separate baths after the dyeing process. High fixation was obtained with a very low K/S value. The moist cotton fibres had a better affinity to the reactive disperse dyes due to the swelling effects and high pH value of the system caused by TEDA [25].

Gao *et al*. [28, 29] synthesised a series of reactive disperse dyes that contained halogenated acetamide and acyl fluoride groups. Application to the dyeing of cotton fabric in supercritical carbon dioxide was carried out without an additive. The colour strength and fastness results were stated to be “reasonably good”. However, compared to the supercritical dyeing of PET, the colour depth needed to be improved. Moreover, there was no clear evidence to show that reaction occurred between dyes and the cotton cellulose.

2.5 Dyeing wool fabric in scCO$_2$

2.5.1 Structure of wool

Wool, the most important commercially available fibre obtained from animals, is classified as a protein aceous fibre. Apart from proteins, raw wool consists of 25-70 % impurities including wool grease, suint, dirt and vegetable matter [89]. The wool investigated in this study was cleaned of all the contaminants.

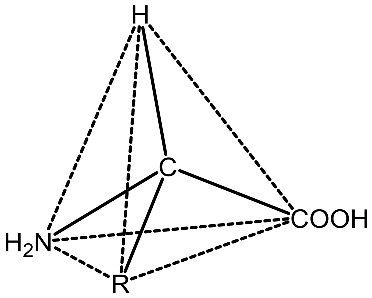
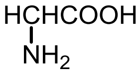
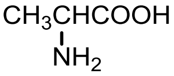
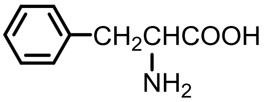
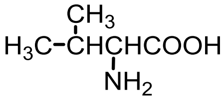
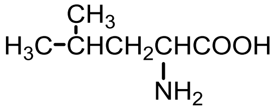
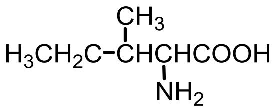
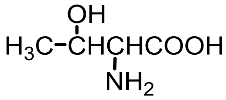
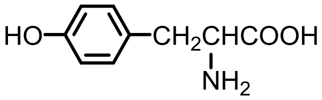
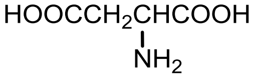
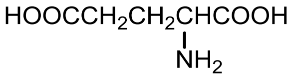
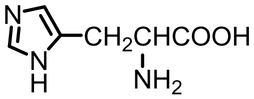
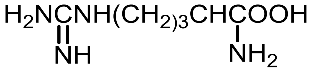
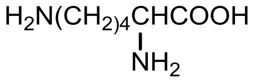
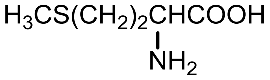
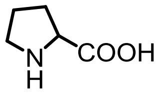


Figure 2.13 General structure of an amino acid

Wool is known as a keratin aceous substrate. Wool contains different types of proteins that have specific structures. Besides a significant sulphur content that comes from the cystine, major structure units of those proteins are amino acid, shown in Figure 2.13 [15, 89, 90]. The amino and carboxyl groups generate dipeptides by condensation reaction. Further condensation reactions may occur between the same or different amino acid groups from dipeptides to form different proteins. More than 20 proteins are found in wool. Table 2.3 shows the formulas and amounts of major amino acids in wool [89].

Table 2.3 Structure and percentage of major amino acids in wool (mol %) [15, 89, 90]

Amino acid	Structure	mol %
Glycine	 $\mathrm{H\underset{NH_2}{C}HCOOH}$	**8.6**
Alanine	 $\mathrm{CH_3\underset{NH_2}{C}HCOOH}$	**5.3**
Phenylalanine	 $\mathrm{-CH_2\underset{NH_2}{C}HCOOH}$	**2.9**
Valine	 $\mathrm{H_3C\text{-}\overset{CH_3}{C}H\underset{NH_2}{C}HCOOH}$	**5.5**
leucine	 $\mathrm{H_3C\text{-}\overset{CH_3}{C}HCH_2\underset{NH_2}{C}HCOOH}$	**7.7**

Isoleucine	 $H_3CH_2C{-}\overset{CH_3}{C}H\underset{NH_2}{C}HCOOH$	**3.1**
Threonine	 $H_3C{-}\overset{OH}{C}H\underset{NH_2}{C}HCOOH$	**6.5**
Tyrosine		**4.0**
Aspartic acid	 $HOOCCH_2\underset{NH_2}{C}HCOOH$	**6.4**
Glutamic acid	 $HOOCCH_2CH_2\underset{NH_2}{C}HCOOH$	**11.9**
Histidine		**0.9**
Arginine	 $H_2N\underset{NH}{\overset{}{C}}NH(CH_2)_3\underset{NH_2}{C}HCOOH$	**6.8**
Lysine	 $H_2N(CH_2)_4\underset{NH_2}{C}HCOOH$	**3.1**
Methionine	 $H_3CS(CH_2)_2\underset{NH_2}{C}HCOOH$	**0.5**
Cystine	 $HOOCH\underset{H_2N}{C}H_2CS{-}SCH_2\underset{NH_2}{C}HCOOH$	**10.5**
Proline		**7.2**

Wool is sensitive to both acidic and basic conditions. Both can cause considerable damage to the wool fibre depending on temperature, duration of exposure, and pH. According to previous research [90], wool is significantly more sensitive to basic solution as the base can potentially remove the surface scales of the wool fibre. Subsequent diffusion of the basic solution into the cortex would degrade the protein structure of the wool by breaking peptide bonds [15].

Wool fibres are hydrophilic and absorb water. This causes radial swelling due to the breakage of inter-chain linkages. Water absorption is an exothermic process due to the formation of hydrogen bonds between the water molecules and the groups in the protein chains. Wool is the most hydrophilic textile fibre and has a moisture regain value between 16-18 %. This is the weight of water absorbed per unit weight of completely dry fibre [23, 90, 91]. Even though wool is somewhat hydrophilic, it is still quite resistant to wetting, largely due to the epicuticle layer, which acts as a barrier [15].

2.5.2 Strategies of dyeing wool using supercritical CO_2

Although the supercritical CO_2 dyeing technology works well for dyeing polyester (PET) fabrics with disperse dyes, it cannot be used for dyeing natural fibres with reactive dyes. As natural fibres such as wool are still one of the more important textile materials for clothing, the inability to apply the supercritical dyeing method to natural fibres has become a stumbling block for the adoption of the supercritical CO_2 dyeing technology by textile dyeing industry. There is an urgent need to develop reactive dyes that can easily dissolve in $scCO_2$ and become covalently bonded to natural fibres. However, so far no successful commercial product has been reported.

Various attempts for dyeing wool in supercritical CO_2 have been made by research groups [18, 92-95]. Schmidt’s results showed that it was possible to dye wool in supercritical CO_2 without pre-treatment of the wool, but colour strength was poor and needed to be improved. Also, the wool fabric was damaged due to extreme dyeing conditions [18]. The aforementioned reverse micellar system was applied not only to the dyeing of cotton but also to the dyeing of wool fabric [93, 95, 96]. Conventional acid dyes were used in this water-pool system where the dyeing would be regarded as low liquor ratio dyeing with highly concentrated dye solution [93]. The dyeing condition for this system is relatively mild, but the dyeing results need to be improved and additives in this system are costly which is not suitable for industry. Van der Kraan *et al*. did some research on wet wool dyeing claiming relatively good results in their publication [92]. To achieve relatively good dyeing quality, high pressure, high temperature and a long dyeing time (230 bar, 112 °C, 2 hours) were required. With the wool fabric saturated with water, higher fixation and colouration results were obtained. The positive effect of water on the dyeing process is caused either by water boosting the reaction between the dye and the fibre or by water acting as a swelling reagent for the textiles [92]. Recently, Long *et al.* developed an eco-friendly method to synthesise three special dyes with dichlorotriazine reactive group [97]. Using dichlorotriazine as the reactive group was the only one capable of dyeing wool. However, the colouration of the dyed wool was not strong enough for industry use due to the introduction of the dichlorotriazine group to the disperse dye, which reduced the solubility of the dye significantly. Therefore, less dye could be dissolved and transported into the wool fibre. In order to achieve a satisfactory colouration and a good fastness, reactive disperse dye having properties of both reactive dye and disperse dye play an important role in this green dyeing procedure of wool. Six different disperse dyes were investigated to explore the most appropriate structure for the modification process of disperse dye [98]. An acceptable colouration and fastness were obtained. Disperse Red 153 and Disperse Blue 148 proved potentially the most promising colourants among the six dyes for reactive modification.

The physical and the chemical effects of supercritical carbon dioxide on polymer fibres during processing are essential research topics of the dyeing process because the impregnation of supercritical fluid many result in different properties and characteristic changes is the fibres which could affect the “quality” of the final product [30, 68]. The plasticisation effect of $scCO_2$ on polyester (PET), is a phenomenon that can improve the mobility of the polymer chain and increase the migration of semi-crystalline polymers like PET [30]. However, natural fabric has relatively higher crystallinity than synthetic fibre. The inability of non-polar and hydrophobic supercritical carbon dioxide to swell polar natural fibres, for example wool and cotton, is one of the bigger obstacles in comparison to the synthetic fibres [30]. Amino groups have been proven to reduce the solubility of chemicals in $scCO_2$ fluid [37]. Thus, the amino groups in wool protein could have a negative effect on the swelling of wool.

2.6 The process and the plant of supercritical fluid technology

The $scCO_2$ dyeing process is an environmentally friendly and commercially available technology that has many merits such as low energy consumption, fast dyeing process and is water free [99]. Despite these merits, manufacturers are unlikely to convert to the $scCO_2$ process due to the high cost. Especially the high initial investment cost and the cost of the maintenance required for the high pressure and high temperature apparatus. Thus, design and construction of the supercritical fluid equipment is essential as these can have a significant effect on the dyeing quality.

In principle, compared to traditional dyeing technology (Table 2.4), there is no additional washing process or drying process in dyeing using supercritical fluids dyeing. No additives are needed either, resulting in the elimination of pollution.

In order to industrialise a new dyeing process and realise the economic benefits, scientists from all over the world have built various dyeing units, from laboratory-scale to pilot-scale.

The development of supercritical dyeing equipment has been slow because of intellectual property protection, there being little communication and lack of cooperation between research organisations. Information based on previous publications regarding plants with the general process of the supercritical dyeing technique is considered here.

According to Bach *et al*. [30], the first real experiment of supercritical dyeing using a special dyeing machine was invented by Jasper GmbH & Co., Velen, Germany, cooperating with the Deutsches Textilforschungszentrum Nord-West e.V. (DTNW) in 1991. After that, a series of developments such as a static dyeing apparatus with a 400 mL autoclave and a stirrable dyeing beam, have been constructed for further research [100]. It was apparent that the stirrable dyeing apparatus achieved a higher dye uptake rate than that in a static condition. Even though there was a stirrer in the autoclave that could improve the dye adsorption, the level dyeing of fibre could not be achieved by this apparatus.

Table 2.4 Comparison of traditional dyeing technology with supercritical dyeing technology

Dyeing process	*Traditional dyeing technology*	*Supercritical dyeing technology*
Washing and reduction	Yes	No
Drying Process	Yes	No
Water	Yes (Mass)	No
Additive	Yes (Mass)	No
Pollute	Yes (Mass)	No
Sewage treatment systems	Yes	No
The remaining dyes	Unrecyclable	Recyclable
Time-consuming	3 to 6 hours	About 1 hour
High pressure	No	Yes

Based on the first trial in the Jasper dyeing plant in 1991, a more practical $scCO_2$ dyeing plant, both at lab and at pilot scale, have been developed to provide good circulation conditions during the dyeing process. UHDE Hochdruchktechnik GmbH, Hagen and DTNW built a new 'fluid recirculation' machine constructed with an extra extraction cycle for removal and separation of excess dyes and spinning oils when dyeing is conducted [30]. The 'fluid recirculation' was proven to have a great influence on the levelness, dye partition and dye exhaustion of supercritical dyeing process by Dews and Eggleston [101]. The whole process is summarised in Figure 2.14. This pilot plant and process was exhibited partly at the International Textile Machinery Exhibition (ITMA 95) in Milan, Italy in 1995 and at ITMA 96 in Osaka, Japan [30]. However, there are some limitations of this revolutionary technology for textile dyeing. For example, the spinning oil and excess dyes could not be extracted thoroughly and clusters or aggregates would present themselves in the supercritical carbon dioxide.

Meanwhile, a supercritical dyeing machine equipped with a single bobbin was designed successfully for PET yarn by the College of Textiles, North Carolina State University, USA [99]. This equipment had a switch to change flow direction, which can improve the levelness of dyeing significantly. Good results were obtained, which were almost the same as water based systems for dyeing PET.

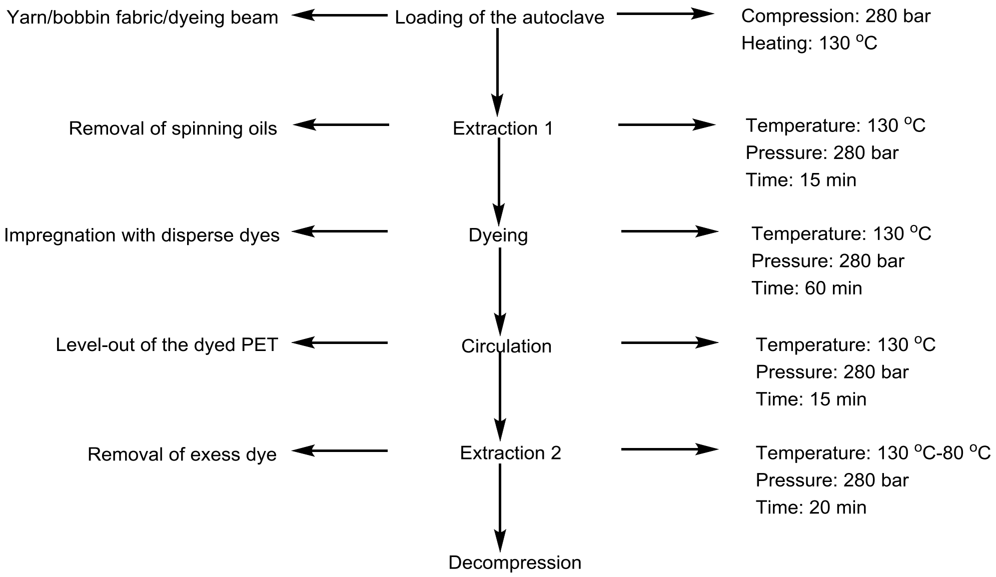


Figure 2.14 Process for dyeing of PET in scCO$_2$

In the early 2000s, researchers from Japan started to design a new generation supercritical dyeing machine. With 630 million Yen support from Japanese government, Hori, *et al.* [102] from Fukui University invented a pilot scale supercritical dyeing plant containing a vessel of 350 L for dyeing of polypropylene and aramids. A significant amount of detailed studies have been conducted by this research group, such as the pre-treatment of fibers with a metal complex during waterless dyeing [99].

In the last decade, many research projects of supercritical dyeing equipment were carried out by researchers in Netherlands. A pilot-scale machine with a 40 L dyeing chamber for fabric beam dyeing was made in 2005 by Delft University of Technology, FeyeCon and its partners. They founded a company named Dyecoo Textile System BC produces supercritical dyeing machines and dyestuffs [100, 103].

According to Dyecoo’s website [103], supercritical dyeing equipment with capacities of 100 - 200 Kg of fabric per batch in an open width of 60 or 80 inches for beam dyeing, supplied by this company, has been employed by Yeh Group of Thailand in 2010 [100, 103]. In addition, Dyecoo established further cooperation with Nike Inc., which has a large share of athletic fabrics for the industrial production of $scCO_2$ dyeing. Therefore, this was the first commercial application for supercritical dyeing [99].

The latest report of a supercritical dyeing plant was published by Long *et al.* [100] who depicted a schematic of a supercritical dyeing system, Figure 2.15, with all subsystems and main equipment. Good fastness results were achieved for the dyeing of synthetic textiles by employing this system and further study has been carried out for dyeing of natural fibres in $scCO_2$.

There are several characterisation methods that can be used during the supercritical dyeing process [44, 76, 81, 100]. The preparation of reactive dyes can be accomplished via organic synthesis. The synthesised compound can be structurally characterised by Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS), and infrared spectroscopy (IR) etc. The etherification kinetics between reactive dyes and methanol can be monitored by High Performance Liquid Chromatography (HPLC) analysis at intervals [44]. The trace elements in the reaction medium can be quantitatively determined by Inductive Coupled Plasma-High Resolution Mass Spectrometry (ICP-HRMS)/Inductive Coupled plasma-Atomic Emission Spectrometry (ICP-AES) analysis. For the dyeing process, especially for cotton, the quality of the dyed pieces of cotton will be determined by means of colour strength measurements and calculation of dye fixation [81]. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric (TG)/differential thermogravimetric (DTG) analysis can be used to investigate the effects of pre-treatments and pressures on textiles, and the plasticisation effects of the polymer after being treated by $scCO_2$ or chemical modification [76, 100].

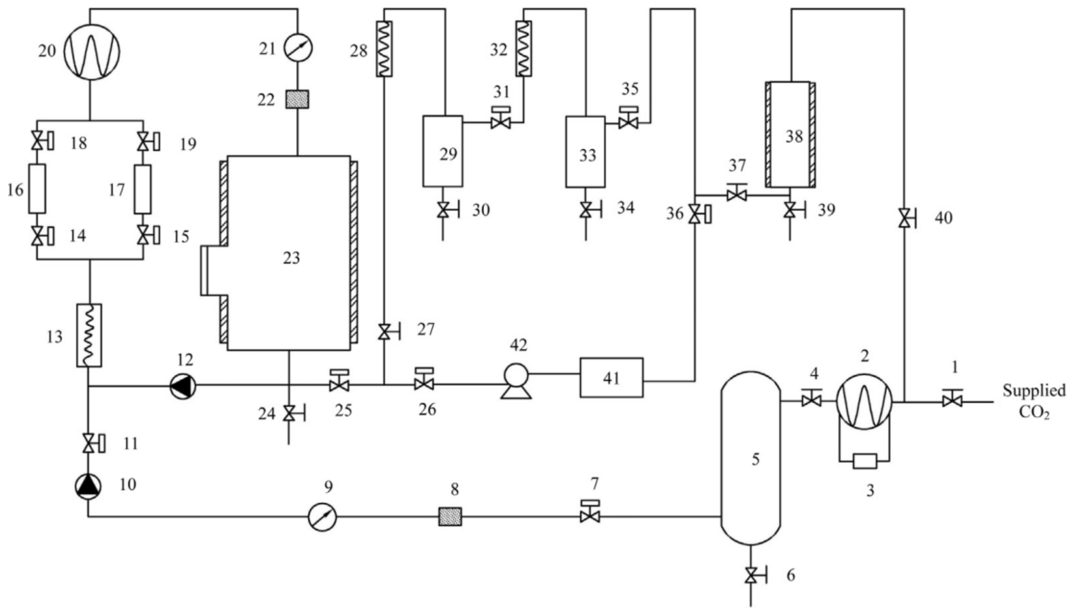


Figure 2.15 Schematic diagram of the pilot scale plant for fabric rope dyeing in supercritical carbon dioxide equipped with (1, 4, 6, 24, 27, 34, 37) stop valves; (2) condenser; (3) cool machine 5) CO_2 storage vessel; (7, 11, 14, 15, 18, 19, 25, 26, 31, 35, 36, 39, 40) electric valves; (8, 22) filter; (9, 21) target flowmeter; (10) pressurization pump; (12) circulation pump; (13, 28, 32) heat exchanger; (16) dyestuff vessel; (17) backup vessel; (20) cooler; (23) dyeing vessel; (29, 33) separator; (38) CO_2 gas purifier; (41) cleaning solvent container; (42) cleaning pump

To realise the industrial application of $scCO_2$ dyeing, many technical challenges need to be addressed with respect to the development of a supercritical fluid plant. First of all, high pressure and high temperature equipment carry high costs, especially for a one-off investment. Alleviation of this problem requires engineering studies specifically those in the material-related field. Secondly, discontinuous feeding is one of the bigger barriers to industrialise the supercritical fluid dyeing in high pressure and high temperature system that results in a longer, more complicated process. Thirdly, phase equilibria and heat transfer of supercritical fluid is much more complicated than that of aqueous systems in such special dyeing conditions. Lastly, the relationship between pilot plant and scale up is not a simple extrapolation. There exists many unknown factors impacting on the dyeing effect, which requires the dyeing process to be optimised before it is put into production.

2.7 Summary

The fundamentals of supercritical dyeing of natural fibres have been presented. The basic concepts of carbon dioxide, dyes, colourimetry and natural fabrics were stated in detail. The latest technologies of dyeing natural fibres in supercritical CO_2 were summarised critically and thoroughly in the review.

The natural fabrics, which have low affinity to disperse dyes and cannot be swollen in $scCO_2$, are the most difficult materials to be dyed in supercritical carbon dioxide. Even though dye uptake and fixation can be enhanced by addition of co-solvent in $scCO_2$ and/or pre-treatment of fibres chemically or physically, the dyeing process still needs to be modified.

It is clear that up until now synthesis of reactive disperse dyes are potentially the most promising approach to dyeing natural fibres in $scCO_2$. The novel approach of modifying disperse dyes with an extremely reactive functional group that can react with the hydroxyl or amine groups on the natural fabrics gives the technique various advantages over the other dyeing technologies discussed. Reactive disperse dyes offer a simple and cheap method of dyeing natural fibres in $scCO_2$ without the excess use of expensive co-solvents, additives and chemical surface modification (pre-treatment). It is for these reasons that the technique is more likely to be utilised on an industrial scale. Even though some of the reactive functional groups presented in the literature for supercritical dyeing have reported good fixation, colour strength and generally good fastness properties, there have been no real observations that any of these groups can adequately dye natural fibres without organic additives.

Thus, in this thesis, major work was focused on developing a series of dyes that would have a good affinity to natural fibre in $scCO_2$ and on the modification of dyeing process.

2.8 References

1. Azdarpour, A., M. Asadullah, E. Mohammadian, H. Hamidi, R. Junin, and M.A. Karaei, *A review on carbon dioxide mineral carbonation through pH-swing process.* Chemical Engineering Journal, 2015. **279**: p. 615-630.
2. Banchero, M., *Supercritical fluid dyeing of synthetic and natural textiles - a review.* Coloration Technology, 2013. **129**(1): p. 2-17.

3. Omae, I., *Recent developments in carbon dioxide utilization for the production of organic chemicals.* Coordination Chemistry Reviews, 2012. **256**(13): p. 1384-1405.
4. Nalawade, S.P., F. Picchioni, and L.P.B.M. Janssen, *Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications.* Progress in Polymer Science, 2006. **31**(1): p. 19-43.
5. Lawton, D., *Carbon capture and storage: opportunities and challenges for geophysics.* CSEG Rec, 2010. **35**(6): p. 7-10.
6. Herrero, M., A. Cifuentes, and E. Ibañez, *Sub- and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae: A review.* Food Chemistry, 2006. **98**(1): p. 136-148.
7. Orr, F. and J. Taber, *Use of carbon dioxide in enhanced oil recovery.* Science, 1984. **224**: p. 563-570.
8. Schollmeyer, E., D. Knittel, H.-J. Buschmann, G.M. Schneider, and K. Poulakis, *Dyeing process*, D. Textilforschungszentrum, Editor. 1990: Germany.
9. Yareite, *Soda bubbles cacro* (online). Accessed 02/02/2017. Available from: https://commons.wikimedia.org/wiki/File:Soda_bubbles_macro.jpg
10. Cai, A., W. Guo, L. Martínez-Rodríguez, and A.W. Kleij, *Palladium-Catalyzed Regio-and Enantioselective Synthesis of Allylic Amines Featuring Tetrasubstituted Tertiary Carbons.* Journal of the American Chemical Society, 2016. **138**(43): p. 14194-14197.
11. Whiteoak, C.J., N. Kielland, V. Laserna, E.C. Escudero-Adán, E. Martin, and A.W. Kleij, *A powerful aluminum catalyst for the synthesis of highly functional organic carbonates.* Journal of the American Chemical Society, 2013. **135**(4): p. 1228-1231.
12. Supercritical, *Food and nutraceutical* (online). Accessed 02/02/2017. Available from: http://89.46.69.105:1105/food-and-nutraceutical/
13. Just-style, *Waterless dyeing garners mixed industry reaction* (online). Accessed 02/02/2017. Available from: http://www.just-style.com/analysis/waterless-dyeing-garners-mixed-industry-reaction_id120351.aspx
14. Lewis, D., *The dyeing of wool with reactive dyes.* Journal of the Society of Dyers and Colourists, 1982. **98**(5-6): p. 165-175.
15. Lewis, D.M., *Wool dyeing*. 1992: Society of Dyers and Colourists.
16. Zollinger, H., *Color chemistry: syntheses, properties, and applications of organic dyes and pigments*. 2003: Wiley. com.
17. Freeman, H.S., L.S. Moser, and W.M. Whaley, *New phosphonic acid reactive dyes for cotton.* Dyes and Pigments, 1988. **9**(1): p. 57-65.
18. Fujioka, S. and S. Abeta, *Development of novel reactive dyes with a mixed bifunctional reactive system.* Dyes and Pigments, 1982. **3**(4): p. 281-294.
19. Renfrew, A. and J. Taylor, *Cellulose reactive dyes: Recent developments and trends.* Coloration Technology, 1990. **20**(1): p. 1-9.
20. Broadbent, A.D., S.o. dyers, and colourists, *Basic principles of textile coloration*. 2001: Society of Dyers and Colorists.
21. Hunger, K., *Industrial dyes*. 2007: Wiley. com.

22. Karst, D. and Y. Yang, *Using the solubility parameter to explain disperse dye sorption on polylactide.* Journal of applied polymer science, 2005. **96**(2): p. 416-422.
23. Schmidt, A., E. Bach, and E. Schollmeyer, *Supercritical fluid dyeing of cotton modified with 2, 4, 6-trichloro-1, 3, 5-triazine.* Coloration technology, 2003. **119**(1): p. 31-36.
24. Schmidt, A., E. Bach, and E. Schollmeyer, *The dyeing of natural fibres with reactive disperse dyes in supercritical carbon dioxide.* Dyes and Pigments, 2003. **56**(1): p. 27-35.
25. Long, J.-J., G.-D. Xiao, H.-M. Xu, L. Wang, C.-L. Cui, J. Liu, M.-Y. Yang, K. Wang, C. Chen, Y.-M. Ren, T. Luan, and Z.-F. Ding, *Dyeing of cotton fabric with a reactive disperse dye in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2012. **69**: p. 13-20.
26. Özcan, A., A. Clifford, K. Bartle, P. Broadbent, and D. Lewis, *Dyeing of modified cotton fibres with disperse dyes from supercritical carbon dioxide.* Journal of the Society of Dyers and Colourists, 1998. **114**(5-6): p. 169-173.
27. Fernandez Cid, M.V., W. Buijs, and G.-J. Witkamp, *Application of molecular modeling in the optimization of reactive cotton dyeing in supercritical carbon dioxide.* Industrial & engineering chemistry research, 2007. **46**(12): p. 3941-3944.
28. Yang, D.-F., X.-J. Kong, D. Gao, H.-S. Cui, T.-T. Huang, and J.-X. Lin, *Dyeing of cotton fabric with reactive disperse dye contain acyl fluoride group in supercritical carbon dioxide.* Dyes and Pigments, 2017. **139**: p. 566-574.
29. Gao, D., H.-S. Cui, T.-T. Huang, D.-F. Yang, and J.-X. Lin, *Synthesis of reactive disperse dyes containing halogenated acetamide group for dyeing cotton fabric in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2014. **86**: p. 108-114.
30. Bach, E., E. Cleve, and E. Schollmeyer, *Past, present and future of supercritical fluid dyeing technology–an overview.* Review of Progress in Coloration and Related Topics, 2002. **32**(1): p. 88-102.
31. Khimeche, K., P. Alessi, I. Kikic, and A. Dahmani, *Solubility of diamines in supercritical carbon dioxide: experimental determination and correlation.* The Journal of Supercritical Fluids, 2007. **41**(1): p. 10-19.
32. Gupta, R.B. and J.-J. Shim, *Solubility in supercritical carbon dioxide*. 2006: CRC press.
33. Tabata, I., J. Lyu, S. Cho, T. Tominaga, and T. Hori, *Relationship between the solubility of disperse dyes and the equilibrium dye adsorption in supercritical fluid dyeing.* Coloration Technology, 2001. **117**(6): p. 346-351.
34. Yamini, Y., M. Moradi, M. Hojjati, F. Nourmohammadian, and A. Saleh, *Solubilities of Some Disperse Yellow Dyes in Supercritical CO_2.* Journal of Chemical & Engineering Data, 2010. **55**(9): p. 3896-3900.
35. Özcan, A.S., A.A. Clifford, K.D. Bartle, and D.M. Lewis, *Solubility of disperse dyes in supercritical carbon dioxide.* Journal of Chemical & Engineering Data, 1997. **42**(3): p. 590-592.
36. Joung, S.N. and K.-P. Yoo, *Solubility of disperse anthraquinone and azo dyes in supercritical carbon dioxide at 313.15 to 393.15 K and from 10 to 25 MPa.* Journal of Chemical & Engineering Data, 1998. **43**(1): p. 9-12.

37. Draper, S., G. Montero, B. Smith, and K. Beck, *Solubility relationships for disperse dyes in supercritical carbon dioxide.* Dyes and Pigments, 2000. **45**(3): p. 177-183.
38. Lee, J.W., M.W. Park, and H.K. Bae, *Measurement and correlation of dye solubility in supercritical carbon dioxide.* Fluid Phase Equilibria, 2000. **173**(2): p. 277-284.
39. Cleve, E., J. Schüttken, E. Schollmeyer, and J. Rucker, *Correlation of solubility data of azo disperse dyes with the dye uptake of poly (ethylene terephthalate) fibres in supercritical carbon dioxide.* Coloration Technology, 2001. **117**(1): p. 13-18.
40. Özcan, A. and A.S. Özcan, *Solubility of an acid dye in supercritical carbon dioxide by ion-pairing with dodecyltrimethylammonium bromide.* Fluid Phase Equilibria, 2006. **249**(1-2): p. 1-5.
41. Gordillo, M., C. Pereyra, and E.M. de la Ossa, *Solubility estimations for Disperse Blue 14 in supercritical carbon dioxide.* Dyes and Pigments, 2005. **67**(3): p. 167-173.
42. Tsai, C.-C., H.-m. Lin, and M.-J. Lee, *Solubility of CI Disperse Violet 1 in supercritical carbon dioxide with or without cosolvent.* Journal of Chemical & Engineering Data, 2008. **53**(9): p. 2163-2169.
43. Zheng, J., X. Mingxian, L. Xueyan, and L. Chunmian, *Measurement and correlation of solubilities of CI disperse red 73, CI disperse blue 183 and their mixture in supercritical carbon dioxide.* Chinese Journal of Chemical Engineering, 2010. **18**(4): p. 648-653.
44. Fernandez Cid, M.V., M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *Kinetics study of a dichlorotriazine reactive dye in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2004. **32**(1-3): p. 147-152.
45. Ellington, J.B., K.M. Park, and J.F. Brennecke, *Effect of local composition enhancements on the esterification of phthalic anhydride with methanol in supercritical carbon dioxide.* Industrial & engineering chemistry research, 1994. **33**(4): p. 965-974.
46. Muthukumaran, P., R.B. Gupta, H.-D. Sung, J.-J. Shim, and H.-K. Bae, *Dye solubility in supercritical carbon dioxide. Effect of hydrogen bonding with cosolvents.* Korean Journal of Chemical Engineering, 1999. **16**(1): p. 111-117.
47. Guzel, B. and A. Akgerman, *Solubility of disperse and mordant dyes in supercritical CO_2.* Journal of Chemical & Engineering Data, 1999. **44**(1): p. 83-85.
48. Tušek, L., V. Golob, and Ž. Knez, *The effect of pressure and temperature on supercritical CO_2 dyeing of PET-dyeing with mixtures of dyes.* International Journal of Polymeric Materials, 2000. **47**(4): p. 657-665.
49. Long, J.J., R.L. Ran, W.D. Jiang, and Z.F. Ding, *Solubility of a reactive disperse dye in supercritical carbon dioxide.* Coloration Technology, 2012. **128**(2): p. 127-132.
50. Shinoda, T. and K. Tamura, *Solubilities of CI disperse orange 25 and CI disperse blue 354 in supercritical carbon dioxide.* Journal of Chemical & Engineering Data, 2003. **48**(4): p. 869-873.

51. Gordillo, M., C. Pereyra, and E. Martínez de la Ossa, *Measurement and correlation of solubility of Disperse Blue 14 in supercritical carbon dioxide.* The Journal of supercritical fluids, 2003. **27**(1): p. 31-37.
52. Coelho, J.P., A.F. Mendonça, A.n.F. Palavra, and R.P. Stateva, *On the Solubility of Three Disperse Anthraquinone Dyes in Supercritical Carbon Dioxide: New Experimental Data and Correlation.* Industrial & Engineering Chemistry Research, 2011. **50**(8): p. 4618-4624.
53. Lin, H.-m., C.-C. Ho, and M.-J. Lee, *Solubilities of disperse dyes of blue 79: 1, red 82 and modified yellow 119 in supercritical carbon dioxide and nitrous oxide.* The Journal of supercritical fluids, 2004. **32**(1): p. 105-114.
54. Tabaraki, R., T. Khayamian, and A. Ensafi, *Wavelet neural network modeling in QSPR for prediction of solubility of 25 anthraquinone dyes at different temperatures and pressures in supercritical carbon dioxide.* Journal of Molecular Graphics and Modelling, 2006. **25**(1): p. 46-54.
55. Park, M.-W. and H.-K. Bae, *Dye distribution in supercritical dyeing with carbon dioxide.* The Journal of supercritical fluids, 2002. **22**(1): p. 65-73.
56. Cabral, V., W. Santos, E. Muniz, A. Rubira, and L. Cardozo-Filho, *Correlation of dye solubility in supercritical carbon dioxide.* The Journal of supercritical fluids, 2007. **40**(2): p. 163-169.
57. Banchero, M., A. Ferri, and L. Manna, *The phase partition of disperse dyes in the dyeing of polyethylene terephthalate with a supercritical CO_2 methanol mixture.* The Journal of Supercritical Fluids, 2009. **48**(1): p. 72-78.
58. Montero, G.A., C.B. Smith, W.A. Hendrix, and D.L. Butcher, *Supercritical fluid technology in textile processing: an overview.* Industrial & engineering chemistry research, 2000. **39**(12): p. 4806-4812.
59. Ferri, A., M. Banchero, L. Manna, and S. Sicardi, *Dye uptake and partition ratio of disperse dyes between a PET yarn and supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2006. **37**(1): p. 107-114.
60. Banchero, M., A. Ferri, and L. Manna, *The phase partition of disperse dyes in the dyeing of polyethylene terephthalate with a supercritical CO_2/methanol mixture.* The Journal of Supercritical Fluids, 2009. **48**(1): p. 72-78.
61. Hirogaki, K., I. Tabata, K. Hisada, and T. Hori, *An investigation of the interaction of supercritical carbon dioxide with poly (ethylene terephthalate) and the effects of some additive modifiers on the interaction.* The Journal of Supercritical Fluids, 2005. **36**(2): p. 166-172.
62. Ryer, A. and V. Light, *Light measurement handbook.* 1997.
63. Newton, I., *Opticks, or, a treatise of the reflections, refractions, inflections & colours of light*. 1979: Courier Corporation.
64. Booth, G., H. Zollinger, K. McLaren, W.G. Sharples, and A. Westwell, *Dyes, general survey.* Ullmann's Encyclopedia of Industrial Chemistry, 2000.
65. Preston, C., *Dyeing of cellulosic fibres*. 1986: distributed by the Society of Dyers and Colourists.
66. Hebeish, A. and J. Guthrie, *The chemistry and technology of cellulosic copolymers*. Vol. 4. 2012: Springer Science & Business Media.
67. Nam, S., A.D. French, B.D. Condon, and M. Concha, *Segal crystallinity index revisited by the simulation of X-ray diffraction patterns of cotton cellulose Iβ and cellulose II.* Carbohydrate polymers, 2016. **135**: p. 1-9.

68. Kikic, I. and F. Vecchione, *Supercritical impregnation of polymers.* Current Opinion in Solid State and Materials Science, 2003. **7**(4): p. 399-405.

69. Mizoguchi, K., T. Hirose, Y. Naito, and Y. Kamiya, *CO_2-induced crystallization of poly (ethylene terephthalate).* Polymer, 1987. **28**(8): p. 1298-1302.

70. Drews, M. and C. Jordan, *The Effect of Supercritical CO_2 Dyeing Conditions on the Morphology of Polyester Fibers.* Textile Chemist & Colorist, 1998. **30**(6).

71. Beltrame, P.L., A. Castelli, E. Selli, L. Villani, A. Mossa, A. Seves, and G. Testa, *Morphological changes and dye uptake of poly (ethylene terephthalate) and 2, 5-cellulose diacetate immersed in supercritical carbon dioxide.* Dyes and pigments, 1998. **39**(1): p. 35-47.

72. Saus, W., D. Knittel, and E. Schollmeyer, *Dyeing of Textiles in Supercritical Carbon Dioxide.* Textile Research Journal, 1993. **63**(3): p. 135-142.

73. Schmidt, A., E. Bach, and E. Schollmeyer, *Damage to natural and synthetic fibers treated in supercritical carbon dioxide at 300 bar and temperatures up to 160 C.* Textile research journal, 2002. **72**(11): p. 1023-1032.

74. Gebert, B., W. Saus, D. Knittel, H.J. Buschmann, and E. Schollmeyer, *DYEING Natural fibres with disperse dye in supecritical carbon dioxide.* Textile Research Journal, 1994. **64**(7): p. 371-374.

75. Beltrame, P.L., A. Castelli, E. Selli, A. Mossa, G. Testa, A.M. Bonfatti, and A. Seves, *Dyeing of Cotton in Supercritical Carbon Dioxide.* Dyes and Pigments, 1998. **39**(4): p. 335-340.

76. Liu, Z.-T., Z. Sun, Z.-W. Liu, J. Lu, and H. Xiong, *Benzylated modification and dyeing of ramie fiber in supercritical carbon dioxide.* Journal of Applied Polymer Science, 2008. **107**(3): p. 1872-1878.

77. Liu, Z.-T., L. Zhang, Z. Liu, Z. Gao, W. Dong, H. Xiong, Y. Peng, and S. Tang, *Supercritical CO_2 dyeing of ramie fiber with disperse dye.* Industrial & engineering chemistry research, 2006. **45**(26): p. 8932-8938.

78. Fernandez Cid, M.V., K.N. Gerstner, J. van Spronsen, M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *Novel Process to Enhance the Dyeability of Cotton in Supercritical Carbon Dioxide.* Textile Research Journal, 2007. **77**(1): p. 38-46.

79. Van der Kraan, Fernandez Cid, M.V., G.F. Woerlee, W.J.T. Veugelers, C. Peters, and G.J. Witkamp, *Equilibrium distribution of water in the two-phase system supercritical carbon dioxide–textile.* The Journal of supercritical fluids, 2007. **40**(3): p. 336-343.

80. Fernandez Cid, M.V., J. van Spronsen, M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *A significant approach to dye cotton in supercritical carbon dioxide with fluorotriazine reactive dyes.* The Journal of supercritical fluids, 2007. **40**(3): p. 477-484.

81. Fernandez Cid, M.V., J. van Spronsen, M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *Excellent dye fixation on cotton dyed in supercritical carbon dioxide using fluorotriazine reactive dyes.* Green Chemistry, 2005. **7**(8): p. 609.

82. Schrell, A. and W.H. Russ, *Process for dyeing aminated cellulose/polyester blend fabric with fiber-reactive disperse dyestuffs*. 1996, Google Patents.

83. Özcan, A., A. Clifford, K. Bartle, P. Broadbent, and D. Lewis, *Dyeing of modified cotton fibres with disperse dyes from supercritical carbon dioxide.* Coloration Technology, 1998. **114**(5-6): p. 169-173.
84. Sawada, K. and M. Ueda, *Adsorption and fixation of a reactive dye on cotton in non‑aqueous systems.* Coloration Technology, 2003. **119**(3): p. 182-186.
85. Saus, W., Hoger, S., Knittel, D., Schollmeyer, E., *Dyeing with supercritical carbon dioxide.* Textilveredlung, 1993. **28**(3): p. 38-40.
86. Maeda, S., S. Hongyou, K. Kunitou, and K. Mishima, *Dyeing Cellulose Fibers with Reactive Disperse Dyes in Supercritical Carbon Dioxide.* Textile Research Journal, 2002. **72**(3): p. 240-244.
87. Sawada, K., T. Takagi, J. Jun, M. Ueda, and D. Lewis, *Dyeing natural fibres in supercritical carbon dioxide using a nonionic surfactant reverse micellar system.* Coloration Technology, 2002. **118**(5): p. 233-237.
88. Jun, J., K. Sawada, and M. Ueda, *Application of perfluoropolyether reverse micelles in supercritical* CO_2 *to dyeing process.* Dyes and Pigments, 2004. **61**(1): p. 17-22.
89. Rippon, J.A., *The structure of wool.* Wool dyeing, 2013: p. 1-51.
90. Simpson, W. and G. Crawshaw, *Wool: science and technology*. 2002: Elsevier.
91. Hearle, J.W. and W.E. Morton, *Physical properties of textile fibres*. 2008: Elsevier.
92. van der Kraan, M., M.V. Fernandez Cid, G.F. Woerlee, W.J.T. Veugelers, and G.J. Witkamp, *Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes.* The Journal of Supercritical Fluids, 2007. **40**(3): p. 470-476.
93. Sawada, K. and M. Ueda, *Evaluation of the dyeing mechanism of an acid dye on protein fibers in supercritical* CO_2*.* Dyes and Pigments, 2004. **63**(1): p. 77-81.
94. Guzel, B. and A. Akgerman, *Mordant dyeing of wool by supercritical processing.* The Journal of Supercritical Fluids, 2000. **18**(3): p. 247-252.
95. Jun, J., M. Ueda, K. Sawada, M. Sugimoto, and H. Urakawa, *Supercritical carbon dioxide containing a cationic perfluoropolyether surfactant for dyeing wool.* Coloration technology, 2005. **121**(6): p. 315-319.
96. Sawada, K. and M. Ueda, *Dyeing of protein fiber in a reverse micellar system.* Dyes and pigments, 2003. **58**(2): p. 99-103.
97. Zhang, Y.-Q., X.-C. Wei, and J.-J. Long, *Ecofriendly synthesis and application of special disperse reactive dyes in waterless coloration of wool with supercritical carbon dioxide.* Journal of Cleaner Production, 2016. **133**: p. 746-756.
98. Zheng, H., Y. Xu, J. Zhang, X. Xiong, J. Yan, and L. Zheng, *An ecofriendly dyeing of wool with supercritical carbon dioxide fluid.* Journal of Cleaner Production, 2017. **143**: p. 269-277.
99. Xing, Y.-J., G. Huang, L. Sheng, J.-K. Sun, and J.-J. Dai, *Development of supercritical* CO_2 *Fluid Dyeing Equipment.* China Textile Leader, 2011(8): p. 79-79.
100. Long, J.-J., H.-M. Xu, C.-L. Cui, X.-C. Wei, F. Chen, and A.-K. Cheng, *A novel plant for fabric rope dyeing in supercritical carbon dioxide and its cleaner production.* Journal of Cleaner Production, 2013.

101. Eggleston, M.J.D.a.J., in *Book of Papers,* AATCC Int. Conf. Exhib., Nashville. 1996: USA. p. 52.
102. Shimbunx, F. Accessed 02/02/2017. *Available from:* www.fukuishimbun.co.jp/modules/feature/index.php?m=200904&author=9.
103. FeyeCon Co., L. *Process and Equipment Technology*(online). Accessed 02/02/2017. Available from: www.feyecon.com/services-and-products/process-and-equipment-technology/equipment-dyeing-systems/.

Chapter 3 Experimental

3.1 Materials

Pure carbon dioxide gas (CO_2>99.9+%; H_2O<20 ppm; O_2<30 ppm) supplied by BOC Gases, UK was used for the supercritical carbon dioxide dyeing of textile fibres. The sourced wool and cotton fabrics were kindly provided by Whaleys (Bradford) Ltd., Yorkshire, UK.

All other reagents used in this study were obtained from the suppliers shown in

Table 3.1 and used without further purification.

Table 3.1 Chemicals used in this study

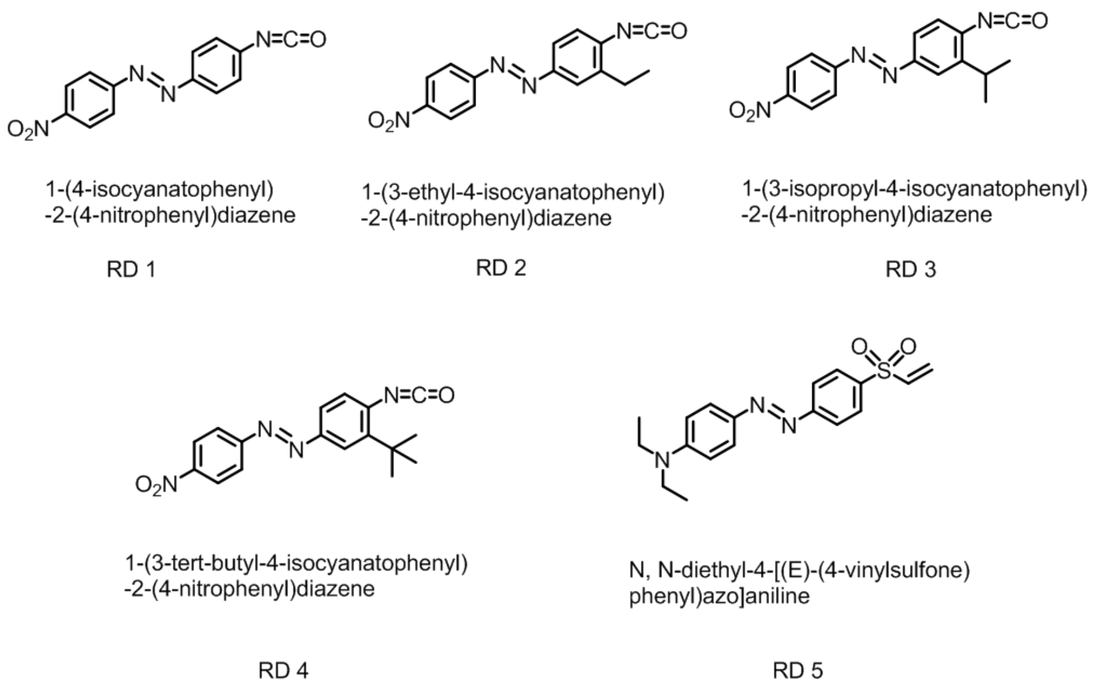
Reagent	***CAS No.***	***Supplier***	***Appearance***	
			Physical State	***Colour***
C.I. Disperse Orange 3	730-40-5	Sigma-Aldrich Co. Ltd.	Solid/powder	Orange
4-Nitroaniline	100-01-6	Fisher Scientific Ltd.	Solid/powder	Yellow
2-Ethylaniline	578-54-1	Fisher Scientific Ltd.	Liquid	Brown
2-Isopropylaniline	643-28-7	Fisher Scientific Ltd.	Liquid	Brown

2-tert-Butylaniline	6310-21-0	Fisher Scientific Ltd.	Liquid	Brown
4-(tert-butyl)-2-nitroaniline	6310-19-6	Apollo Scientific	Solid/powder	Orange
4-Aminobenzenethiol	1193-02-8	Fluorochem Ltd.	Solidified mass or fragments	Yellow
2-chloroethanol	107-07-3	Merck, KGaA	Liquid	Colourless
Oxone	70693-62-8	Fluorochem Ltd.	Granular	White
Methanesulfonyl chloride	124-63-0	Acros Organics	Liquid	Colourless
N,N-Diethylaniline	91-66-7	Acros Organics	Liquid	Yellow
Triethylamine	121-44-8	Fisher Chemical	Liquid	Colourless
Cyanuric chloride	108-77-0	Acros Organics	Powder	White
Aluminium oxide(activated, neutral)	1344-28-1	Sigma-Aldrich Co. Ltd.	Powder	White
Sodium nitrite	7632-00-0	Fisher Scientific Ltd.	Solid/powder	Colourless

Hydrochloric acid (37.2 %)	7647-01-0	Fisher Scientific Ltd.	Liquid	Colourless
Diphosgene	503-38-8	Alfa Aesar	Liquid	Light yellow
Potassium carbonate	584-08-7	Fisher Scientific Ltd.	Solid/powder	Colourless
Magnesium sulfate - anhydrous	7487-88-9	BDH Chemicals Ltd.	Powder	White
Sodium chloride	7647-14-5	Fisher Chemical	Powder	White
Sodium hydroxide	1310-72-2	Fisher Scientific Ltd.	Solid/pellets	White
Sodium bicarbonate	144-55-8	Sigma-Aldrich Co. Ltd.	Powder	White
Sodium carbonate (anhydrous)	497-19-8	Vickers Laboraory Ltd.	Powder	White
Chloroform-d	865-49-6	Sigma-Aldrich Co. Ltd.	Liquid	Colourless

3.2 Dye preparation

The reactive disperse dyes used in this research were synthesised in-house. The structures of these dyes are shown in Figure 3.1 and a complete description of the dye synthesis is given. Disperse Reactive Dyes 1, 2, 3 and 4 (RD 1, RD 2, RD 3 and RD 4) are based on the isocyanate reactive group that has a high reactivity to hydroxyl and amine groups. Moreover RD 2, RD 3 and RD 4 potentially have high solubility in $scCO_2$ due to the introduction of the alkyl groups onto the chromophore. Reactive Disperse Dye 5 (RD 5) contains vinyl sulphonyl reactive groups, and has been shown to have good dyeing affinity to both cotton and wool [1, 2]. Each of the synthesis procedures has the potential to be easily scaled up in industry. All of the synthesised compounds achieved industrial grade without purification.



1-(4-isocyanatophenyl)
-2-(4-nitrophenyl)diazene

RD 1

1-(3-ethyl-4-isocyanatophenyl)
-2-(4-nitrophenyl)diazene

RD 2

1-(3-isopropyl-4-isocyanatophenyl)
-2-(4-nitrophenyl)diazene

RD 3

1-(3-tert-butyl-4-isocyanatophenyl)
-2-(4-nitrophenyl)diazene

RD 4

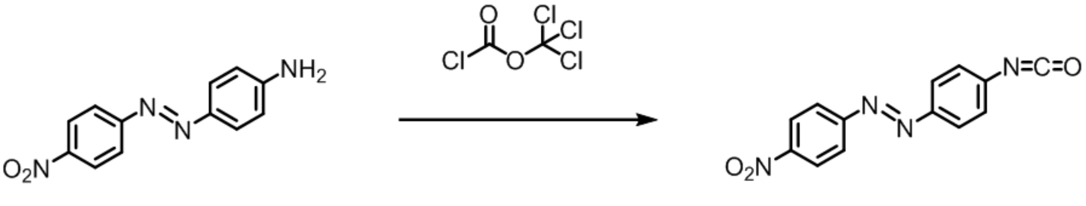
N, N-diethyl-4-[(E)-(4-vinylsulfone)
phenyl)azo]aniline

RD 5

Figure 3.1 Reactive disperse dyes synthesised during this research

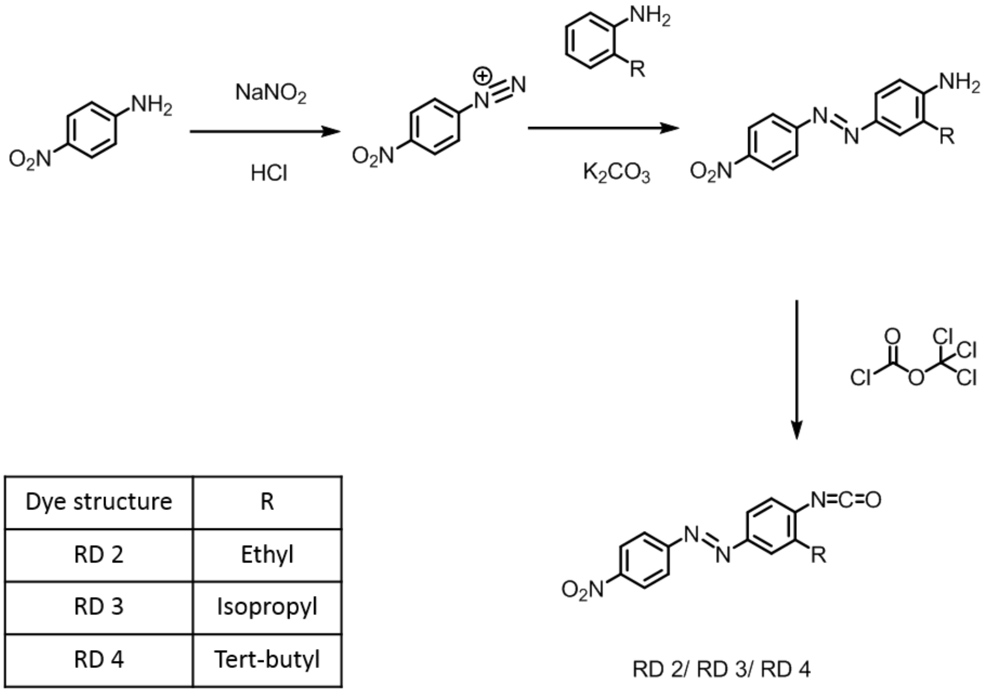
3.2.1 Procedure for the synthesis RD 1

The general procedure for synthesising the reactive disperse dyes is shown in Scheme 3.1. To a 250 mL three-neck round-bottom flask equipped with a reflux condenser, C.I. Disperse Orange 3 (4.12 mmol, 1 g) in 100 mL distilled THF and a magnetic stirring bar were added. Diphosgene (8.14 mmol, 1 mL) was added dropwise over 10 minutes. The reaction temperature was maintained at 60 °C for 10 hours and the reaction progress monitored by TLC. The mixture was concentrated to dryness on a rotary evaporator. Red solid compound was obtained, (78 %), (RD 1) [3].


RD 1

Scheme 3.1 General procedure for synthesis of 1-(4-isocyanatophenyl)-2-(4-nitrophenyl)diazene (RD 1)

3.2.2 Procedure for synthesis of RD 2, RD 3 and RD 4



Dye structure	R
RD 2	Ethyl
RD 3	Isopropyl
RD 4	Tert-butyl

RD 2/ RD 3/ RD 4

Scheme 3.2 General procedure for the synthesis of the highly CO_2 soluble disperse reactive dyes with isocyanate group

3.2.2.1 Preparation of 2-methyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine, 2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine and 2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

4-nitroaniline (2.76 g, 20 mmol) was dissolved in a mixture of conc. HCl (10 mL) and distilled water (40 mL). A solution of sodium nitrite (1.66 g, 24 mmol) in distilled water (10 mL) was then prepared. The sodium nitrite solution was added dropwise to the acidic amine solution over a period of 5 minutes at 0 °C. The resulting mixture was stirred at 0 °C for 40 minutes, forming a benzene diazonium salt solution [4].

The nitrobenzene diazonium salt solution was injected dropwise into a stirred solution of either 2-tert-butylaniline/2-ethylaniline/2-isopropylaniline (20 mmol) under nitrogen at 0 °C. The pH of the mixture was kept between 6 and 7 through the addition of the appropriate amount of deoxygenated K_2CO_3 (1 M) solution. The reaction mixture was then stirred under nitrogen at 0 °C for 30 minutes leading to precipitation of the product. Precipitation was driven to completion through the addition of a few drops of dilute HCl (10 %). The precipitate was extracted with diethyl ether and evaporated to dryness under reduced pressure to leave the corresponding crude disperse dye molecule (2-ethyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine/2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine/2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine). The crude product was purified by recrystallisation with 10:1 ethonal-water to give the corresponding disperse dye as a red brown solid (68 %/ 75 %/ 78 %).

3.2.2.2 Preparation of RD 2, RD 3 and RD 4

The synthesised disperse dye ((2-ethyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine/2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine/2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine)) (4.12 mmol) was added to THF (50 mL) and trichloromethylformate (1.0 mL, 8.28 mmol). The mixture was stirred and heated at 55-60 °C under nitrogen for 15 hours. The heating discontinued after 15 hours. The solvent was evaporated leaving the RD 2 with the ethyl group/RD 3 with the isopropyl group/ RD 4 with the tert-butyl group (88 %/ 86 %/ 93 %) as a red brown solid [3].

3.2.3 Procedure for the synthesis of RD 5

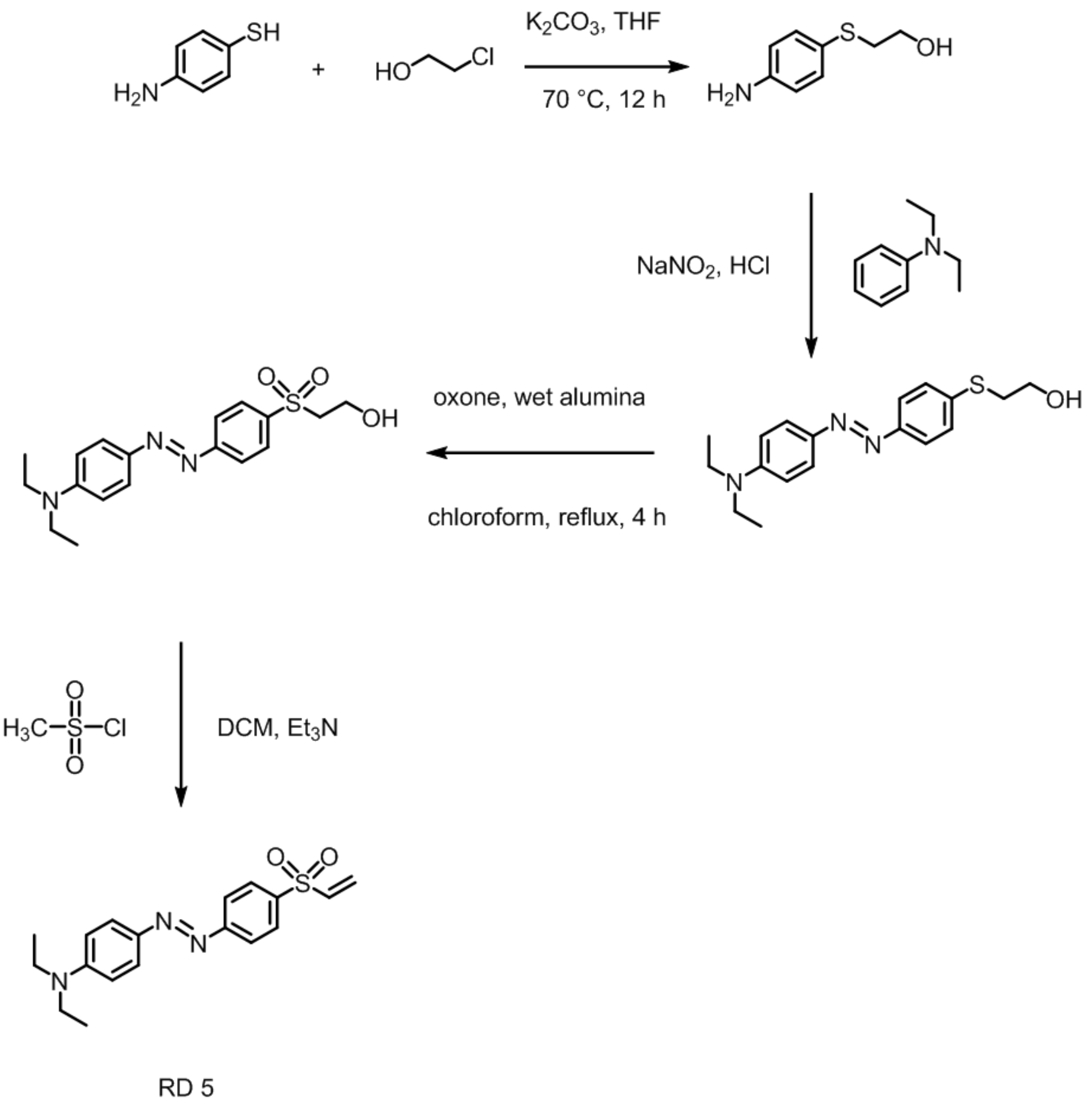


Figure 3.2 Synthesis route of the Reactive Disperse Dye (5)

The synthesis route given as Figure 3.2 provides a general method to synthesise the vinyl sulphone based reactive disperse dye. In this study, the target RD 5 was synthesised, starting from the coupling component aniline containing 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 sulphone functional group. Methanesulphonyl chloride was used to bind through the hydroxyl on compound to increase the leaving ability of the hydroxyl group. In the presence of a base, the vinyl sulphone disperse dye was produced via elimination. In contrast to the synthesis of traditional reactive dyes, reactive disperse dyes are synthesised in non-aqueous conditions. It was possible to carry out the whole procedure without any purification after each step.

3.2.3.1 Preparation of 2-[(4-aminophenyl)sulphanyl]ethanol

Aminobenzene-1-thiol (5.0 g, 40.0 mmol) and potassium carbonate (11.06 g, 80.0 mmol) were added to THF (250 mL) and stirred. The solution was cooled to 0 °C using an ice bath and 2-chloroethanol (2.94 mL, 44.0 mmol) was then added dropwise. The mixture was left to reflux at 70 °C for 12 hours. The THF was removed under reduced pressure. DCM (3 x 30 mL) was added and the organic layers were separated off and combined, washed with water (30ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give of 2-[(4-aminophenyl)sulphanyl]ethanol (82 %) as a colourless oil; product was deemed sufficiently pure to carry on the synthesis routes without further purification [5].

3.2.3.2 Preparation of N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo] aniline

2-[(4-Aminophenyl)sulphanyl]ethanol (3.02 g, 17.8 mmol) was dissolved in water (100 mL) and concentrated HCl (25 mL). The solution was cooled to 0 °C using an ice bath. Sodium nitrite (1.6 g, 21.4 mmol), in water (25 mL) was added dropwise over 5 minutes. The mixture was then stirred for 40 minutes. As the diazonium salt formed, the solution changed from black to bright orange. In a separate flask N,N-diethylaniline (2.65 g, 17.8 mmol) was added to glacial acetic acid (20 mL) and water (15 mL), the mixture deoxygenated and placed under an inert nitrogen atmosphere. The flask was cooled to 0 °C and the diazonium solution was added using a syringe. The pH was changed to 7 using a deoxygenated 1 M solution of potassium carbonate. The reaction mixture was stirred for 30 minutes. The solution remained bright orange. The solution was acidified using HCl (10 % v/v) and the mixture was stirred for 10 minutes. The little precipitate that had formed was filtered and the filtrate was stored for 2 days. Dark red precipitate formed on the bottom of the flask. DCM (3 x 30 mL) was added and the organic layers were separated off and combined, washed with water (30 mL) and dried ($MgSO_4$). Solvent was removed under reduced pressure to give the azo dye (86 %) as dark red granules [4, 6]. The product was deemed sufficiently pure to use without further purification.

3.2.3.3 Preparation of N, N-diethyl-4-[((4-sulphonylethanol)phenyl)azo] aniline

N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo]aniline (1.45 g, 4.41 mmol) was added to a solution of oxone (4.06 g, 13.23 mmol) and wet alumina (7.5 g) in chloroform (60 mL). The mixture was refluxed at 100 °C for 4 hours. The solution was allowed to cool before being filtered and the precipitate was washed thoroughly with chloroform. Solvent was dried (Mg_2SO_4) and removed under reduced pressure to give N, N-diethyl-4-[((4-sulphonylethanol)phenyl)azo]aniline (85 %) as a red wet solid. The product was deemed sufficiently pure to use without further purification [7].

3.2.3.4 Preparation of N, N-diethyl-4-[((4-vinylsulfone)phenyl)azo]aniline, RD 5

N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo]aniline (1.37 g, 3.80 mmol) was dissolved in DCM (50 mL) and cooled to 0 °C using an ice bath. Methanesulphonyl chloride (0.35 mL, 4.60 mmol) and triethylamine (1.59 mL, 11.40 mmol) were added dropwise at 0 °C. The reaction was left to stir at room temperature for 12 hours. TLC showed the reaction had yet to go to completion. Triethylamine (1.59 mL, 11.40 mmol) was added and the mixture was left to reflux at 80 °C for 2 hours. Water (20 mL) and DCM (3 x 20 mL) was then added and the organic layers were separated off and combined, washed with 10 % $NaHCO_3$ solution (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the vinyl sulphone dye (72 %) as red flakes [5].

3.3 Supercritical CO_2 system

A continuous supply CO_2 apparatus (Figure 3.3), for dyeing fabrics in $scCO_2$, in the Wolfson CO_2 Laboratory of the University of Leeds was used in the dyeing experiments. A 20 mL high pressure view cell, (Figure 3.4) was previously designed and built by researchers of the School of Mechanical Engineering, University of Leeds. The cell was divided into a body and a lid. Two 15 mm thick borosilicate glass windows were set, one in the body and the other in the lid. The internal of the cell chamber could be viewed through these windows. Three pipe threads (inlet, outlet and thermometer connection) entered the cell at the top. A stirrer hotplate was placed at the bottom of the cell, allowing heating/cooling and stirring, (Figure 3.5). Figure 3.6 shows this components of the laboratory scale plant for supercritical dyeing.

Figure 3.3 Photograph of the high pressure CO_2 supply system (1) central control panel; (2) high pressure pumps; (3) chiller

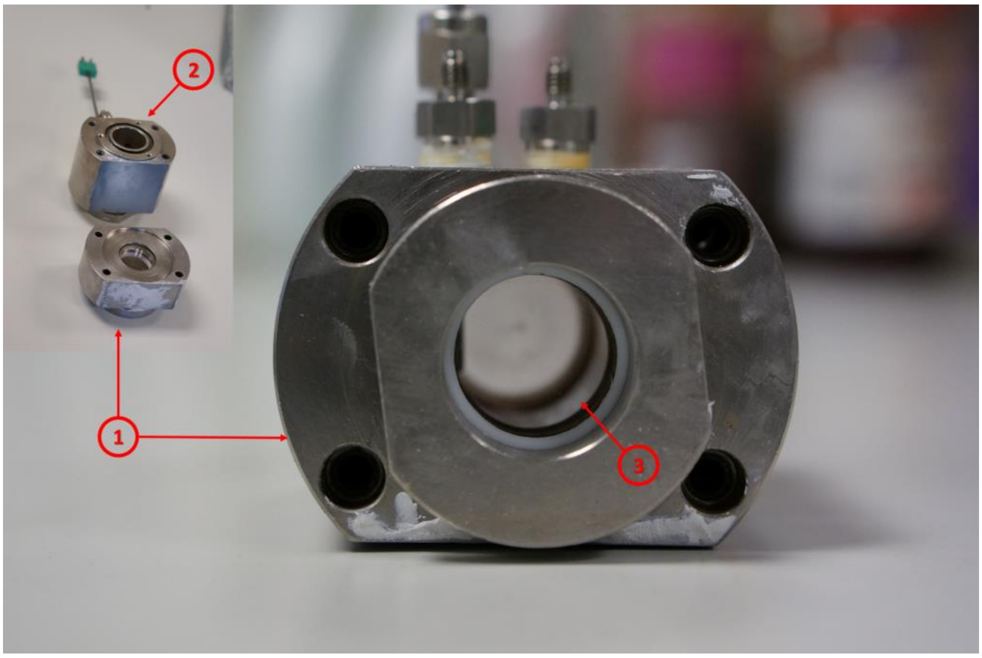


Figure 3.4 Photograph of the high pressure viewing cell (1) cell lid; (2) cell body; (3) 15 mm thick borosilicate glass window

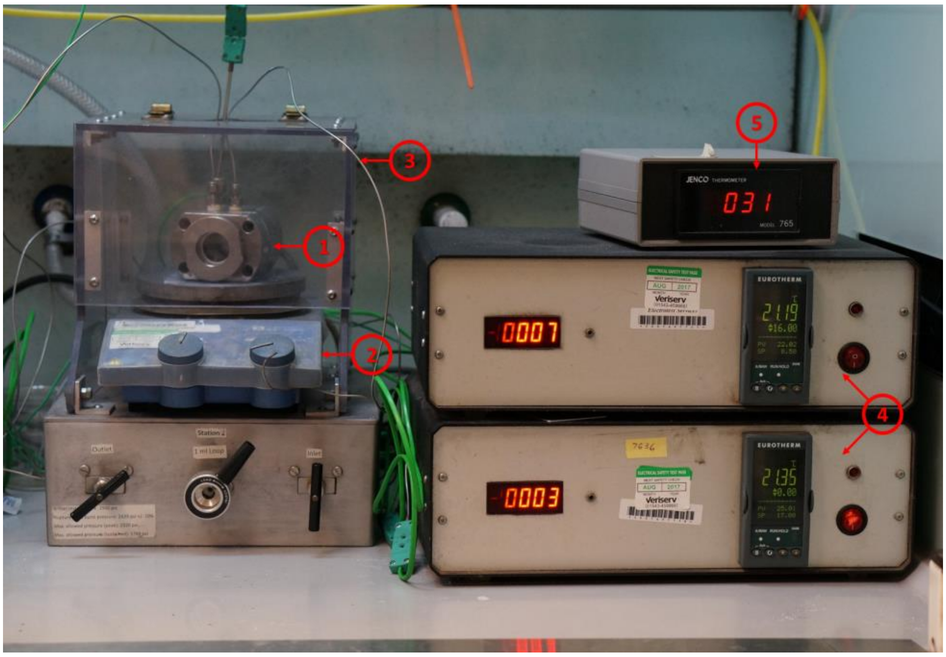


Figure 3.5 Photograph of the supercritical dyeing control system (1) high pressure view cell; (2) stirrer hotplate; (3) polycarbonate shield; (4) pressure display and control; (5) temperature display

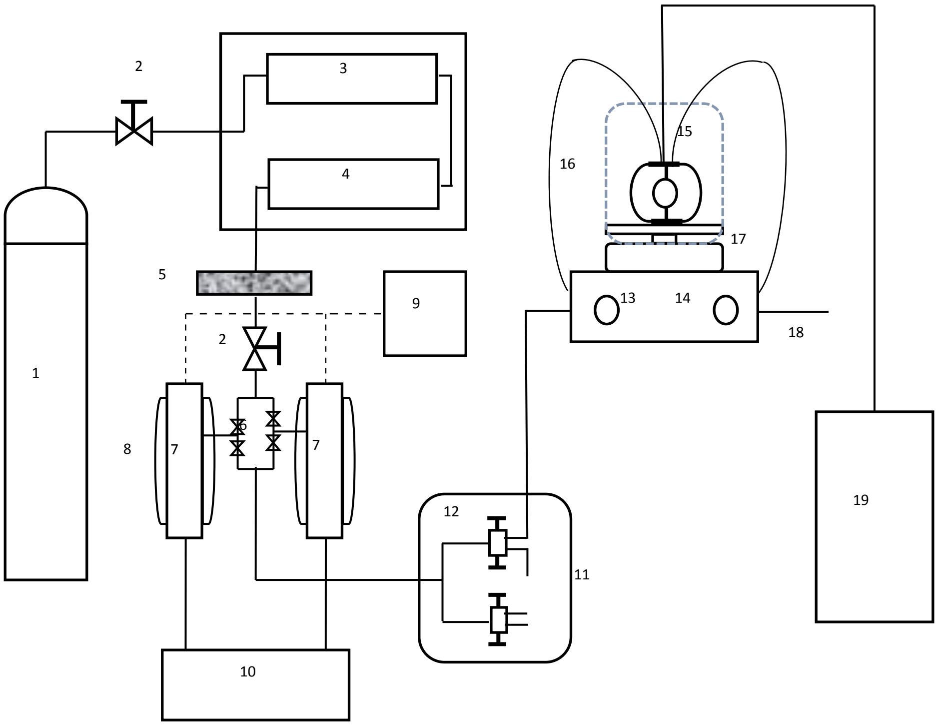


Figure 3.6 Schematic diagram of the lab scale plant for fabric dyeing in supercritical carbon dioxide equipped with (1)cylinder; (2) stop valves; (3) H_2O scavenger; (4) O_2 scavenger; (5) filter; (6) electronically controlled valves; (7) syringe pumps; (8) cooling jacket; (9) chiller; (10) pump controller; (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) pressure display and temperature control; (19) outlet tubing

3.4 General dyeing procedure in supercritical carbon dioxide

3.4.1 Water pre-treatment

Water pre-treatment of the fabrics was carried out at room temperature in the atmosphere for 30 minutes. 3 % owf. excessive water was used to penetrate fabric in order to garrentee that most water is still avaliable after 30 minutes of evaporation. For example, when 30 % owf. of water was used to pre-treat a piece of fabric, 33 % owf. of water was added initially. After 30 minutes, around 3 % owf. of water was removed by evaporation. The amount of water that remained on the fabric after pre-treatment was controlled before dyeing.

3.4.2 General procedure for supercritical dyeing

A piece of fabric (100 ± 0.1 mg) was placed at the bottom of the cell together with 4 % on the weight of fabric (owf.) of fine dye powder and a stirrer bar. After the cell was sealed, the system was pressurised to 40 bar with CO_2 using a pair of Isco 260D syringe pumps. The temperature was maintained at 90 °C and the pressure was increased slowly to 140 bar. Heating was stopped when the dyeing process finished. The reactor was depressurised by gradually opening the outlet valve. This helped the temperature to decrease to 45 °C. The cell was then opened and the sample retrieved.

3.5 Colour measurement

3.5.1 Colour strength

Figure 3.7 Photograph of the Minolta spectrophotometer

The colour strength of the supercritical dyed natural fabrics was described by the K/S value of the fabrics, which is determined by the Kubelka–Munk equation (Equation 3.1). 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) (Figure 3.7).

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

Equation 3.1 Kubelka-Munk equation

The K/S value at R_{min} is directly proportional to the loading of dye in 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 better correlate with the visual evaluation of the sample than would 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 Equation 3.2. Here λ, is wavelength [1].

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

Equation 3.2 Definition of f_k value

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

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

Equation 3.3 Definition of *F* value

3.5.2 Colour characterisation

A Minolta spectrophotometer (model CR3600d; Minolta Co., Japan) was used to measure the reflectance of dyed fabrics, to characterise the colour of the dyed samples, under standardised lighting conditions (D65). CIE $L^*a^*b^*$ measurements were implemented, and L^* (lightness), a^* (green-red), and b^* (blue-yellow) of chromaticity were used for the test. Three randomly selected locations on each dyed fabric surfaces were analysed and averaged [8].

3.6 Wash fastness

In the wash fastness tests, the change/fade in colour of the dyed cotton fabric and also any staining of colour on the adjacent undyed fabric were assessed. All of the experimental methods were carried out according to the BS ISO 105-C06:2010 [9]. Thus, specimens (6.5 x 6.0 cm) were attached to adjacent fabric of SDC Multifibre DW (acetate, cotton, polyamide, polyester, acrylic and wool), and a grade 3 water with appropriate detergent was prepared. The specimens and detergent solution were added into a 150 mL flask with a stirring bar (specimen attached with multifibre: detergent : water = 1 : 2.5 : 50). The system was stirred at 40 °C for 1 hour. The fabrics was washed three times using grade 3 water and dried at room temperature, under standard atmospheric conditions until the mass no longer changed.

A standard grey scale, with grades between 1 and 5 was used in assessing the colourfastness to washing. Grade 5 has two identical greys, with grade 1 on grey scale representing the largest contrast, and the rest of the grades having intermediate contrasts. After appropriate treatment aforementioned, the specimen was compared with the original untreated material. Any fade or change in colour was graded with reference to the grey scale. If there was no change in the colour characteristics of a test specimen, it was identified as '5'; if there was a change then it was classified with the number of the scale that corresponded with the same contrast as that between the treated specimens and the untreated specimens.

A set of grey scales was used for measuring staining. A fastness rating of 5 was shown by two identical white samples (no staining). Rating 1 showed a white and a grey sample. The other numbers showed steps of contrast between white and the series of greys. A piece of untreated, unstained, undyed cloth was compared with the treated sample that had been in contact with the test specimen during the staining test and a numerical assessment of staining was given. A rating of 5 showed that there was no difference between the treated sample and the untreated material. If the result was in between any two of the contrasts on the scale, a rating of, for example, 3-4 was given. Sets of grey scales, examples of which are shown in Figure 3.8 were supplied by the Department of Colour Science, School of Chemistry, University of Leeds.

Colour assessment was carried out under standardised lighting conditions (D65), in a dark room.

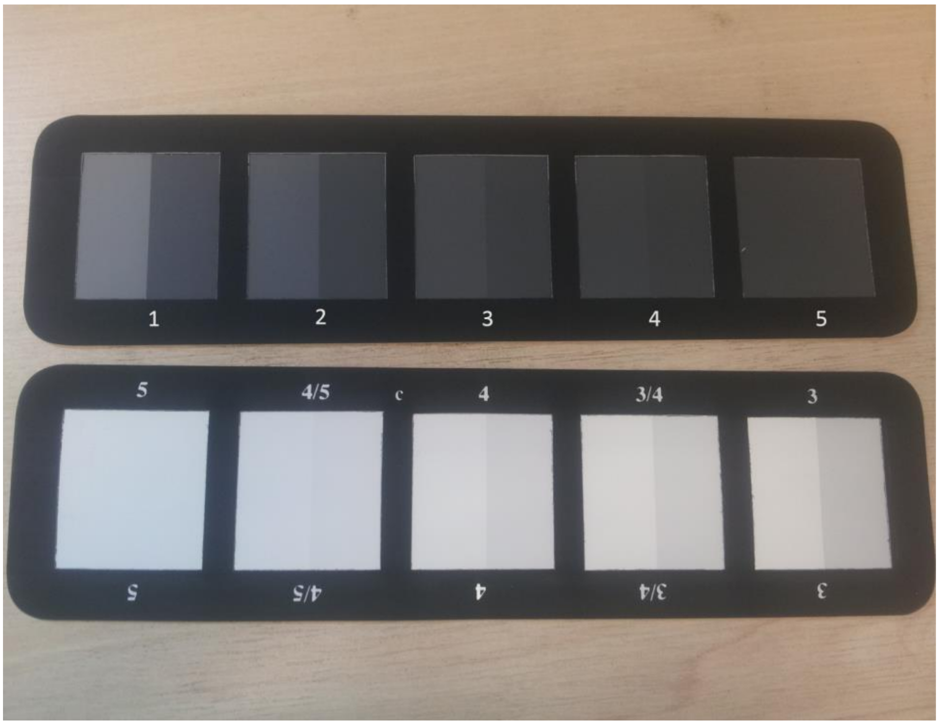


Figure 3.8 Photograph of the grey scales. The upper scale was the Colour Change Grey Scale; the lower scale was the Degree of Staining Grey Scale

3.7 Microscopy study

SEM was used to gain a better understanding of the effect of $scCO_2$ on the surface physical properties of the dyed fabric. SEM is a widely used technique. In this, a focused beam of electrons is scanned across the surface of an electrically conductive specimen. A Jeol JSM-6610LV model SEM (Figure 3.9) 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 conductive carbon tape. The dyed fibre sample was then gold-coated using a Bio-Rad SC500 diode sputter coating unit, (Figure 3.10). 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.

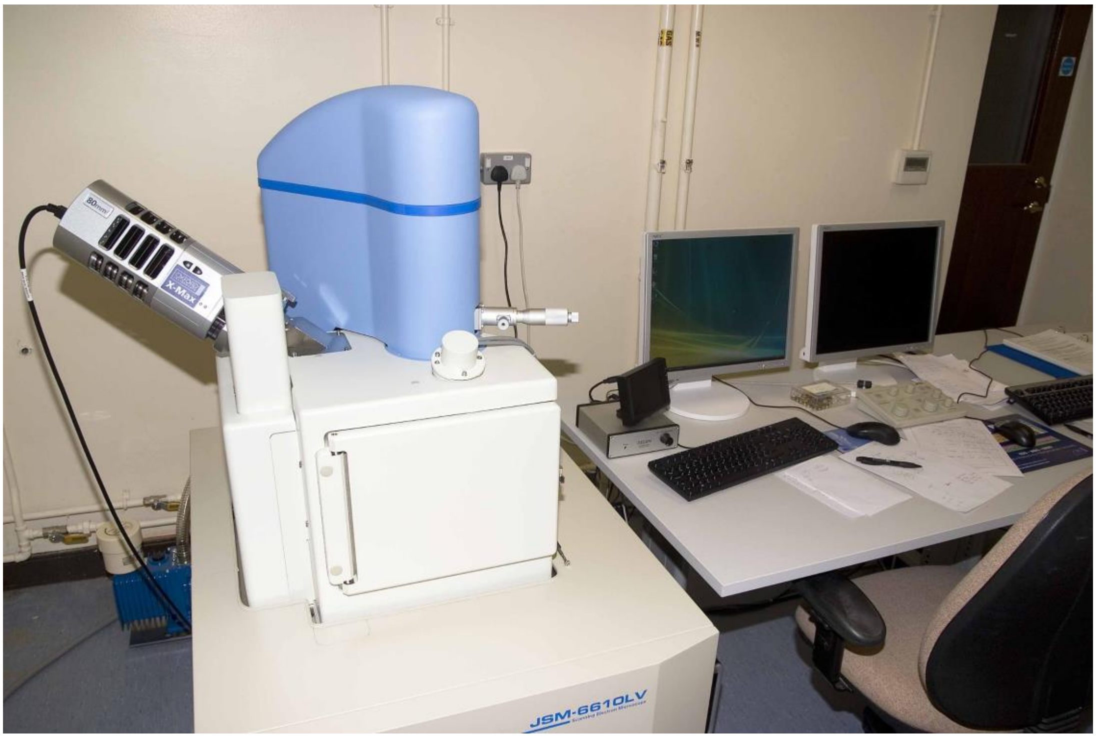


Figure 3.9 Photograph of the Jeol JSM-6610LV model SEM

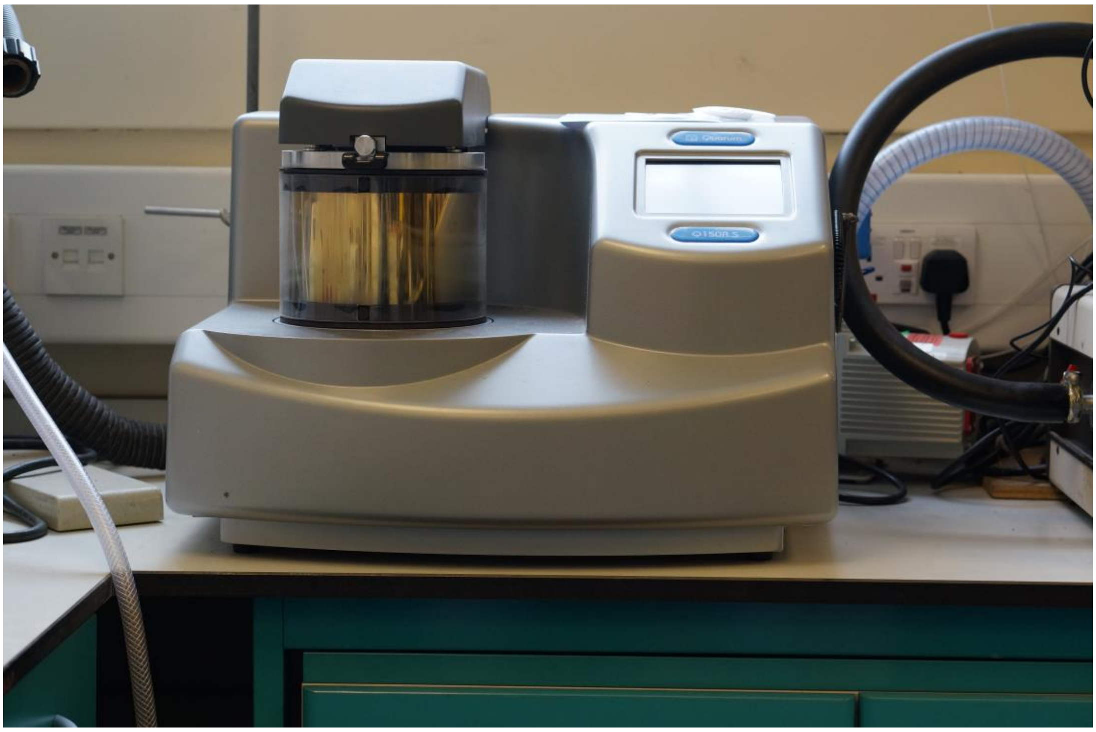


Figure 3.10 Photograph of the Bio-Rad SC500 diode sputter coating unit

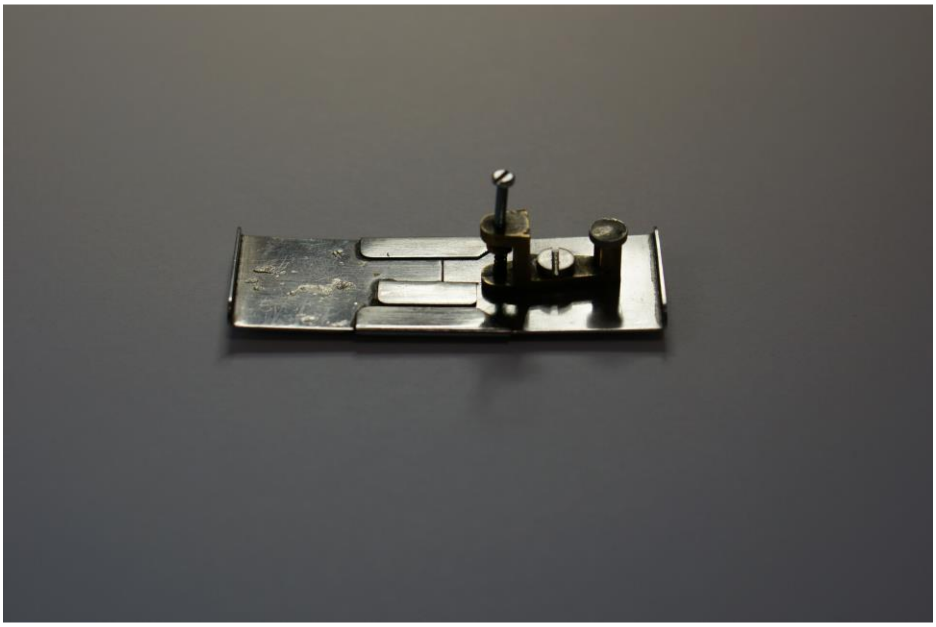


Figure 3.11 Photograph of the Hardy Microtone

Figure 3.12 Photograph of the Vickers M41 Microplan

For optical microscopy studies, a Hardy Microtone (Figure 3.11) was used to cut cross-sections of dyed samples. A Vickers M41 Microplan optical microscope (Figure 3.12) was used to magnify the cross-sections [10]. The photomicrographs were recorded using a Vickers M41 Photoplan (fitted with a x25 objective and a x2.5 eyepiece) coupled to a Nikon D90 Digital Single Lens Reflex camera via a Hama T2 microscope adapter.

3.8 References

1. Lewis, D.M. and L.T. Vo, *Dyeing cotton with reactive dyes under neutral conditions.* Coloration Technology, 2007. **123**(5): p. 306-311.
2. Lewis, D.M., *Dyeing wool with reactive dyes.* The Coloration of Wool and other Keratin Fibres, 2013: p. 251-290.
3. Sigurdsson, S.T., B. Seeger, U. Kutzke, and F. Eckstein, *A mild and simple method for the preparation of isocyanates from aliphatic amines using trichloromethyl chloroformate. Synthesis of an isocyanate containing an activated disulfide.* Journal of organic chemistry, 1996. **61**(11): p. 3883-3884.

4. Haghbeen, K. and E.W. Tan, *Facile synthesis of catechol azo dyes.* The Journal of Organic Chemistry, 1998. **63**(13): p. 4503-4505.
5. Lee, J.W., Son, H. J. and Jung, Y. E, *A Practival and Large Scale Synthesis of Phenyl Vinyl Sulfone from Benzenethiol and 2-Chloroethanol.* Bulletin of the Korean Chemical Society, 1995. **16**(7): p. 670-672.
6. Johnson, P.S., C. Huang, M. Kim, N.S. Safron, M.S. Arnold, B.M. Wong, P. Gopalan, and F. Himpsel, *Orientation of a monolayer of dipolar molecules on graphene from X-ray absorption spectroscopy.* Langmuir, 2014. **30**(9): p. 2559-2565.
7. Greenhalgh, R.P., *Selective oxidation of phenyl sulphides to sulphoxides or sulphones using Oxone® and wet alumina.* Synlett, 1992. **1992**(03): p. 235-236.
8. Kim, S.-J., D.-K. Kim, and D.-H. Kang, *Using UVC light-emitting diodes at wavelengths of 266 to 279 nanometers to inactivate foodborne pathogens and pasteurize sliced cheese.* Applied and environmental microbiology, 2016. **82**(1): p. 11-17.
9. ISO, Textiles-Tests for colour fastness-Colour fastness to domestic and commercial laundering, British Standards Institution(BSI Group), London, UK, 2010.
10. Asquith, R.S., *Chemistry of natural protein fibers*. 2012: Springer Science & Business Media.

Chapter 4 Dyeing natural fabrics with reactive disperse dye containing isocyanate reactive group in supercritical $scCO_2$

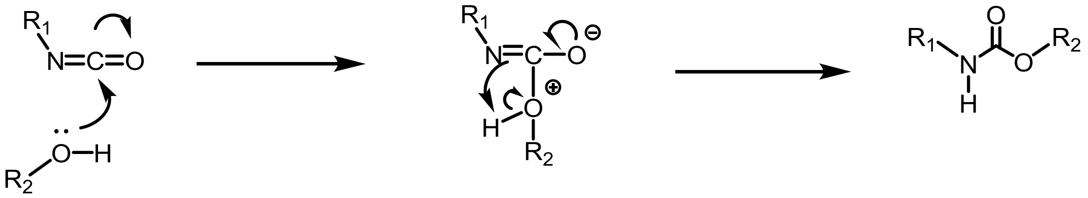
4.1 Introduction

4.1.1 Background

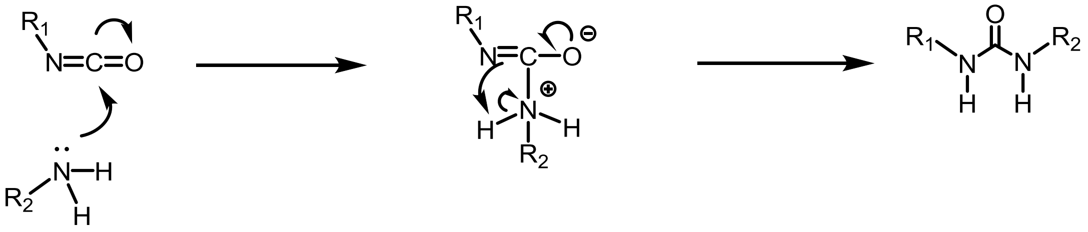
The supercritical dyeing of natural fabrics is a environmentally-friendly technology that has become increasingly popular in recent years. In this study, wool fabrics and cotton fabrics were dyed with an isocyanate-group modified disperse dye, using supercritical dyeing technology.

Isocyanate groups have been widely used in polymer syntheses and in industry since the Bayer Company proved that elastomeric polyurethanes were formed from the reaction of toluene diisocyanate with polyfunctional alcohols [1]. Isocyanates are electrophiles, and as such they are reactive toward a variety of nucleophiles including alcohols and amines. The development of isocyanates for fibre modification usage was also an important step in fibre treatments [2-4]. The isocyanate group was also introduced as a reactive group for dyes due to its high reactivity [5, 6]. However, this functional group, which is known to have an affinity for cellulosic structures such as cotton (containing hydroxyl group) and wool (containing amino acid function), has not been used as a reactive group in a dye molecule for supercritical dyeing previously. Even though the isocyanate functionality may not be suitable for traditional water dyeing due to it being toxic and very sensitive to water, it still can form substituted ureas and urethane linkages very effectively with amine groups and alcohol groups respectively upon reaction within the atmosphere of the $scCO_2$ dyeing vessel [7].

The mechanisms of the isocyanate reaction with hydroxyl group and with amine groups are depicted in Scheme 4.1 and Scheme 4.2 respectively.



Scheme 4.1 Mechanism of an isocyanate group reacting with a hydroxyl group



Scheme 4.2 Mechanism of an isocyanate group reacting with an amine group

4.1.2 Rationale

One objective of this project was to synthesise reactive disperse dyes that can be of use in the dyeing industry. The aim was to find a highly reactive group that was able to react with amino groups or hydroxyl groups, without additives, and also be stable when attached to a chromophore group. The isocyanate group was selected as the reactive group due to its excellent reactivity with the hydroxyl groups and amino groups. C.I. Disperse Orange 3 as a commercial azo disperse dye was chosen as the chromophoric molecule because of its strong colour density and relatively high solubility in $scCO_2$ [8]. Moreover, the free amino group of Disperse Orange 3 can be easily modified to isocyanate group. Thus, the RD 1 (characterisation is presented in Chapter 7) depicted in Figure **4.1**, was synthesised as a model compound used to test the reactivity of the isocyanate group towards cotton and wool.

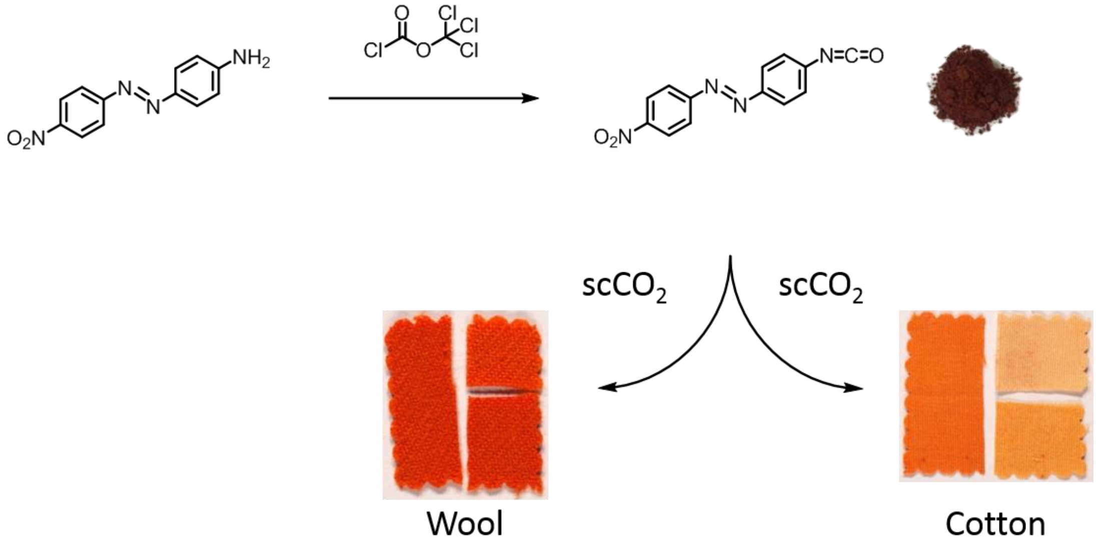


Figure 4.1 Graphical abstract of Chapter 4

Supercritical dyeing experiments using RD 1 were carried out below 140 bar. These resulted in the production of dyed wool that showed excellent colour strength, fixation and wash fastness following 20 minutes of dyeing. Microscopy studies revealed that the high pressure dyeing did not cause much fibre damage. Compared with other supercritical dyeing methods, the mild conditions of this supercritical dyeing process, with disperse dyes containing the isocyanate group has some commercial potential.

4.2 Results and discussion

4.2.1 Dyeing wool fabric using RD 1 containing isocyanate reactive group

4.2.1.1 Investigation of the effect of temperature on the dyeing of wool, using RD 1 containing isocyanate reactive group

The influence of the reaction temperature on the effectiveness of wool dyeing was investigated at 140 bar, using 4 % owf. of RD 1 and 60 minutes of dyeing time for dry wool fabric (Figure 4.2A) and for wet wool fabric (20 % owf. of water addition in the pre-treatment process), (Figure 4.2B).

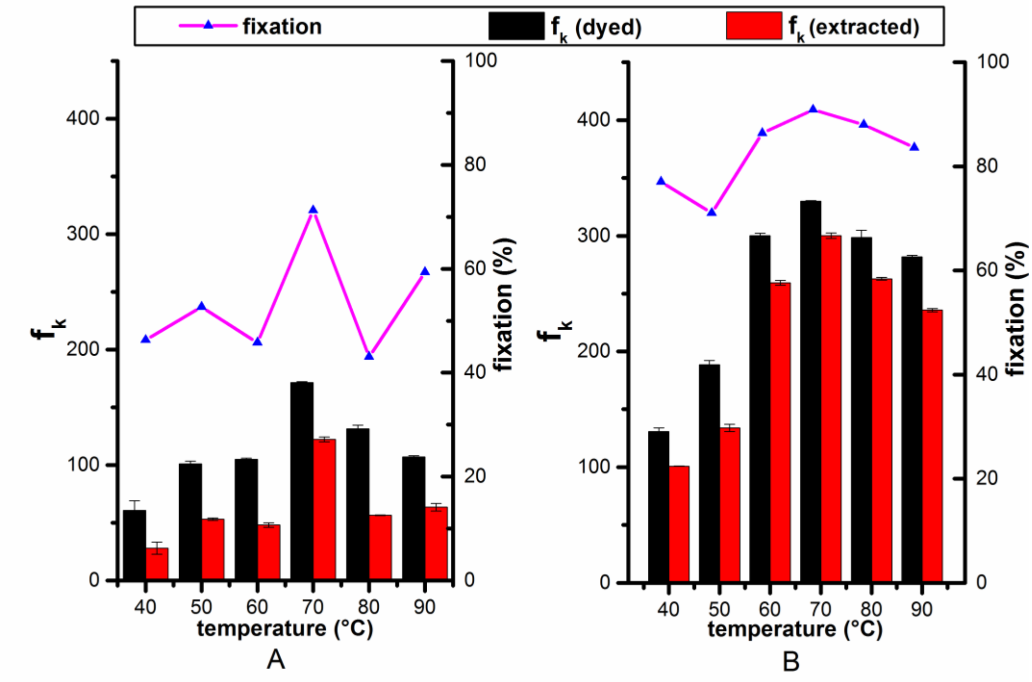


Figure 4.2 Effect of the system temperature on the f_k value and the dye fixation of (A) dry wool (B) wet wool (20 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 4 % owf. of RD 1, at 140 bar, for 60 minutes

It can be seen from the Figure 4.2 that the colouration f_k value and the fixation of the dyed wet wool were greater than those of dry wool. The f_k value first increased until the temperature reached 70 °C and decreased with a further increase in temperature, especially for the extracted wool fabric. Two major factors can be responsible for this phenomenon, namely the solubility and the mobility of the dyes in $scCO_2$, contributing to the f_k value, when the temperature is changed at a constant pressure. Increasing the dyeing temperature at a constant pressure decreased the density of $scCO_2$ and consequently decreased the solubility of the dye in $scCO_2$. However, greater diffusivity and mobility of the $scCO_2$ can be obtained at higher temperatures, allowing enhanced transportation of the dye from $scCO_2$ to the fabrics.

According to Figure 4.2, the colour and fixation of dyed fabrics were most affected by the reactivity of the synthesised dye increase. A decrease in the dye solubility had a greater impact on the colouration and fixation of dyed fabric than the mobility increase of the dye. The balance of f_k value between decreasing the solubility, decreasing the viscosity, increasing the diffusivity and potentially increasing the reactivity, can be achieved at 70 °C. The greatest fixation (94.3 %) and good colouration [$f_{k(\text{dyed})} = 292.0$] of the dry wool and of the wet wool were obtained at 70 °C.

4.2.1.2 Investigation of the effect of pressure on the dyeing of wool, using RD 1 containing isocyanate reactive group

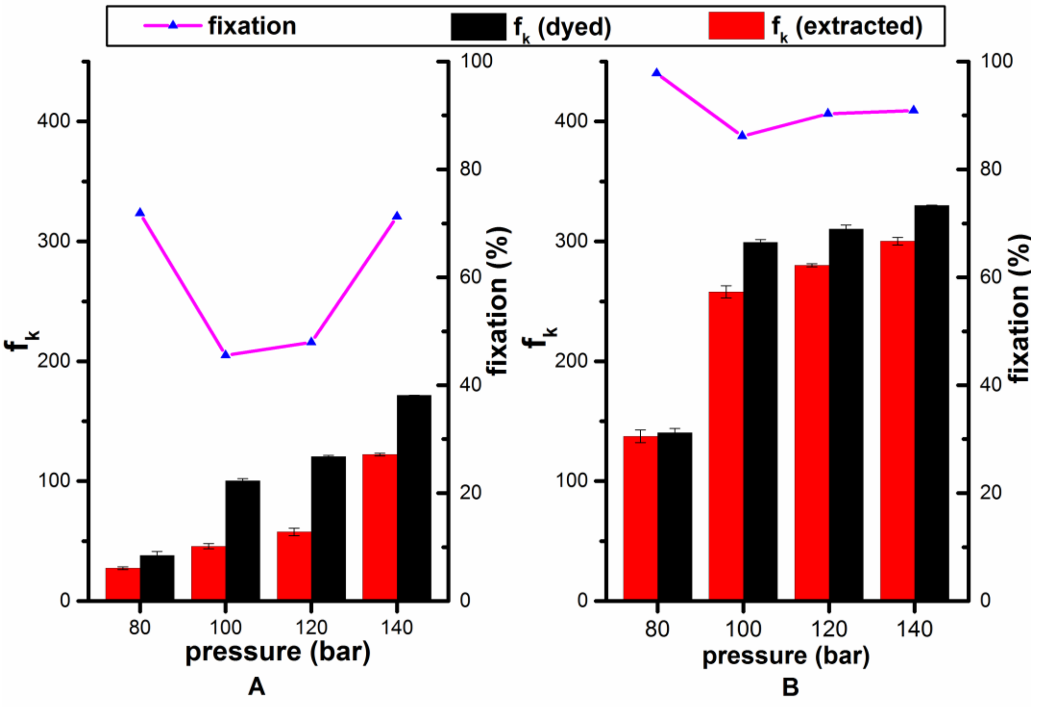


Figure 4.3 Effect of system pressure on the f_k value and on the dye fixation of (A) dry wool (B) wet wool (20 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 4 % owf. of RD 1, at 70 °C, for 60 minutes

In Figure **4.3**, the results are given for various reaction pressures (from 80 to 140 bar) for the dyeing of dry wool and of wet (20 % owf.) wool with 4 % owf. of RD 1, at 70 °C, for 60 minutes. The density of the $scCO_2$ and the solubility of dye in $scCO_2$ increased with pressure at constant temperature, resulting in enhanced colouration and fixation of dye on the wool. The greatest fixation rate of both dyed dry wool and dyed wet wool was obtained at 80 bar. This was because most of the dye molecules were not dissolved in $scCO_2$, meaning that there were few dye molecules that diffused into the wool fabric, and most of these molecules reacted with the amino groups in the fabric. The dye fixation of the dyed wet wool fabric increased linearly up to 94.3 %, when the pressure was increased from 100 bar to 140 bar. Figure **4.3**A shows that the colouration of dyed dry wool was dependent on pressure linearly. For the 20 % owf. water pre-treated wool fabric (Figure **4.3**B), the colouration increased considerably from 80 bar to 100 bar, but approached a steady $[f_{k(dyed)} = 300 \pm 10]$ as the pressure increased above 100 bar. This indicates that the wet wool was almost saturated with dye molecules above 100 bar.

4.2.1.3 Investigation of the effect of dye loading on the dyeing of wool using RD 1 containing isocyanate reactive group

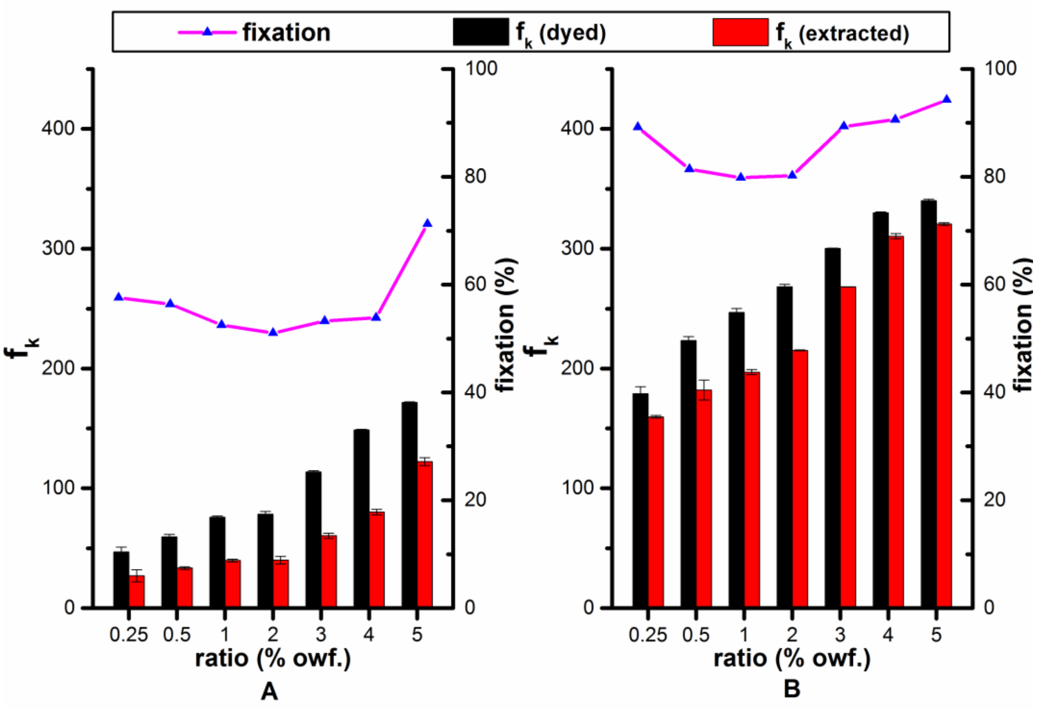


Figure 4.4 Effect of different loadings of RD 1 on the f_k value and on dye fixation of (A) dry wool (B) wet wool, (20 % owf. of water pre-treated for 30 minutes), dyed in scCO$_2$, at 70 °C, 140 bar, for 60 minutes

The effect of varying the dye loading on the dyeing process was investigated (Figure **4.4**). The reaction vessel contained one of the following loadings 0.25 %, 0.5 %, 1 %, 2 %, 3 %, 4 %, 5 % owf. of dye, with the dyeing experiments being carried for 60 minutes at 70 °C and 140 bar. As the dye loading was increased, the colouration of both the dyed dry wool and the dyed wet wool improved. The $f_{k(dyed)}$ values shown in Figure **4.4**A were very poor compared to the results shown in Figure **4.4**B. For the dry wool, the highest $f_{k(dyed)}$ value was obtained at the dye loading of 5 % owf., which was the same as the lowest value of the wet wool dyed at the dye loading of 0.25 % owf. Figure **4.4**B indicates that the strongest colouration [$f_{k(dyed)} = 300 \pm 10$] of dyed wet wool (20 % owf. of water addition in the pre-treatment process) was obtained by raising the dye loading to 5 % owf. From the $f_{k(dyed)}$ results, it is clear that greater dye loading resulted in more intense wool colouration. The highest fixation rate of the dyed wet wool was 94.3 % with 5 % owf. of dye at 70 °C, 140 bar during 60 minutes of dyeing. The phenomenon shown in Figure **4.3** has also been observed here, with a high fixation rate being obtained at low dye loading, but poorly coloured.

4.2.1.4 Investigation of the effect of pre-treatment water amount on the dyeing of wool, using RD 1 containing isocyanate reactive group

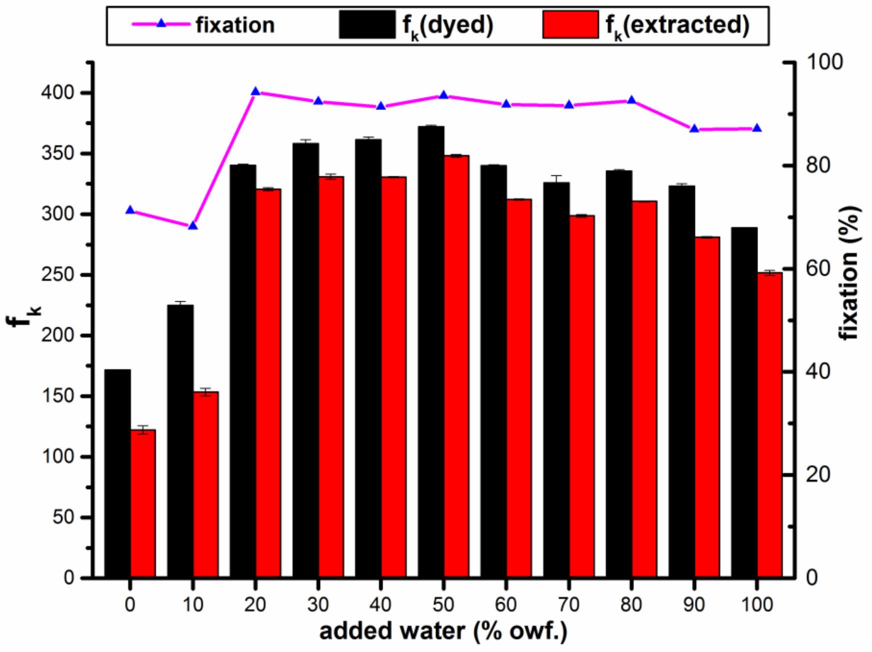


Figure 4.5 Effect of water addition, in the pre-treatment process on the f_k value and on the dye fixation on wet wool dyed in scCO$_2$ with 5 % owf. of RD 1 at 70 °C, 140 bar, for 60 minutes

According to the data that show the effect of temperature, pressure and dye loading on wool colour in scCO$_2$, dry wool dyeing in scCO$_2$ improved dramatically by water pre-treatment. Water in the wet dyeing system played a positive role in the wool fabric swelling, assisting the interaction between the dye and the wool. In Figure 4.5, the results are given for dyeing at varying amounts of water used in the pre-treatment process (from 0 % to 100 % owf.) with 5 % owf. of RD 1 at 70 °C, 140 bar for 60 minutes. The colouration was enhanced at water loading of less than 80 % but diminished at loadings over 80 %. The fixation rate of dyed wet wool was excellent at the water loadings from 20 % to 100 % owf. The highest fixation value was obtained at 50 % owf.

4.2.1.5 Investigation of the effect of dyeing time on the dyeing of wool, using RD 1 containing isocyanate reactive group

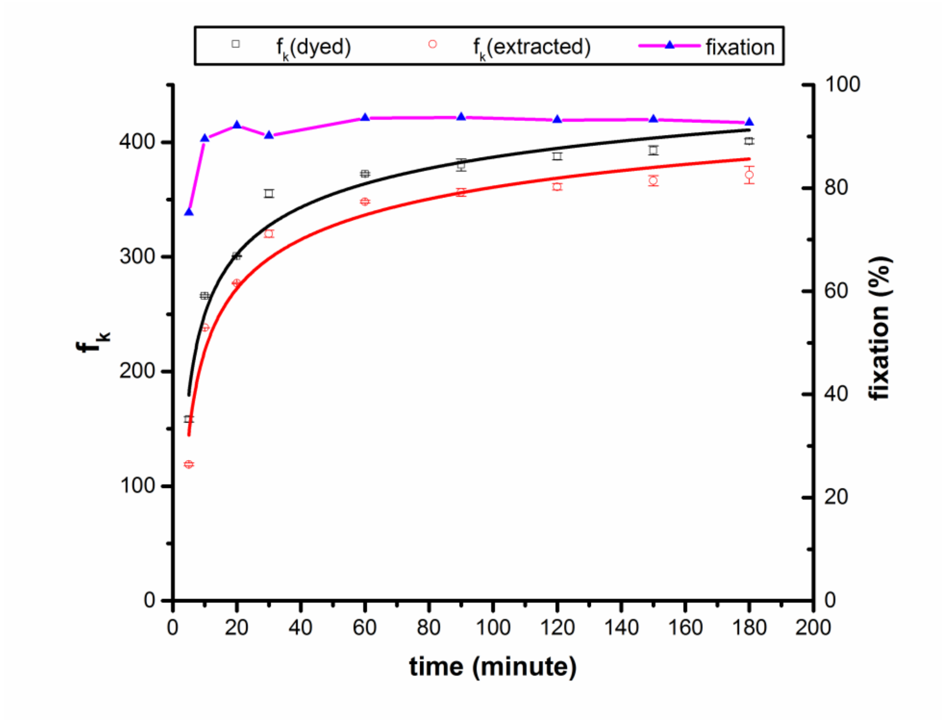


Figure 4.6 Effect of dyeing time on the f_k value and on the dye fixation of wet wool (20 % owf. of water, pre-treated for 30 minutes), dyed in scCO$_2$ with 5 % owf. of RD 1, at 70 °C, 140 bar

The effect of dyeing time on the dyeing properties of wet wool was examined with 50 % owf. of water in the pre-treatment process, 5 % owf. of dye at 70 °C, 140 bar (Figure 4.6). The fixation reached 89.5 % after only 10 minutes dyeing time. The $f_{k(dyed)}$ value increased rapidly to 300.7 after 20 minutes, before reaching 400.9 after 180 minutes. The $f_{k(dyed)}$ value was stable after 60 minutes. The fixation decreased after 60 minutes as shown by the increasing $f_{k(dyed)}$ value and the steady $f_{k(extracted)}$ value. Thus, the functional sites of wool reacted with a high proportion of the dye molecules after 60 minutes.

4.2.1.6 Colour fastness testing

The wash fastness of wool fabrics coloured with 5 % owf. of dye, 50 % owf. of water in scCO$_2$, at 70 °C, 140 bar for various dyeing times was measured (Table 4.1). The tests were carried out according to the BS ISO 105-C06:2010 [9]. Excellent staining fastness was obtained due to the high reactivity of the dye, which achieved the requirements of a commercial product. The minor cross colour on the adjacent multifibre is due to dye on the surface of the wool fabric having not reacted with the fibre. A small amount of surface dye was removed by washing, and was transferred to the adjacent multifibre. The fading fastness was less than the staining fastness, especially for samples with insufficient dyeing times.

Table 4.1 The fastness data of wool fabrics pre-treated with 50 % owf. of water, coloured with 5 % owf. of RD 1, in scCO$_2$ at 70 °C, 140 bar at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	3-4	3-4	5	4-5	4	4	4-5
20	4	4	5	4-5	5	4-5	4-5
60	5	4	5	5	5	4-5	4-5
180	5	5	5	5	5	4-5	5

4.2.2 Dyeing cotton fabric using RD 1 containing isocyanate reactive group

4.2.2.1 Investigation of effect of temperature on the dyeing of cotton, using RD 1 containing isocyanate reactive group

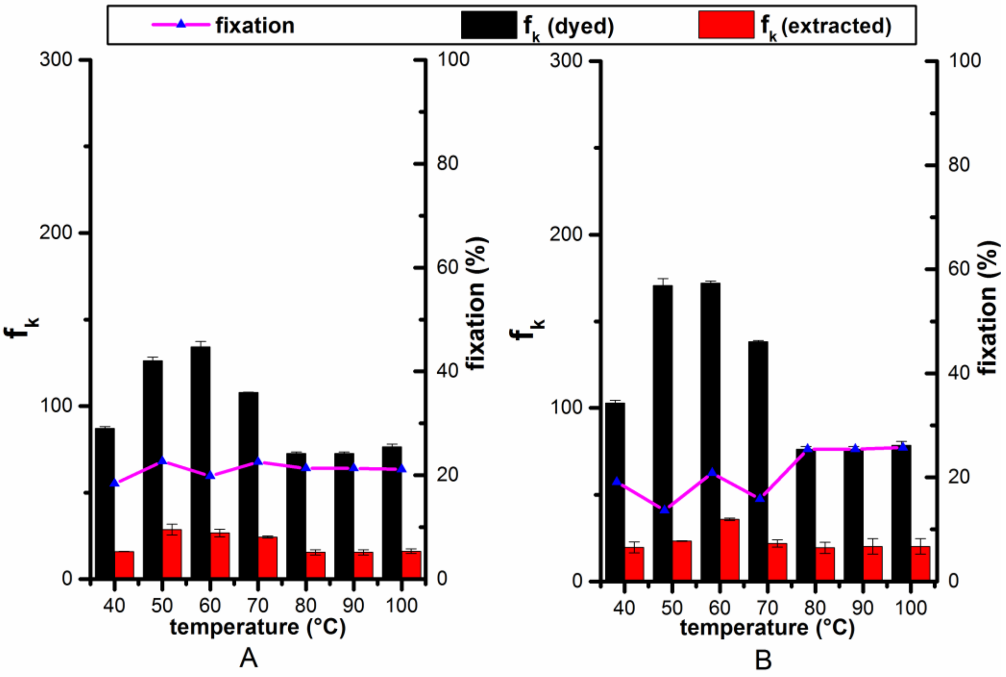


Figure 4.7 Effect of the temperature on the f_k value and on the dye fixation of (A) dry cotton (B) wet cotton (20 % owf. of water pre-treated for 30 minutes), dyed in scCO$_2$ with 5 % owf. of RD 1, at 140 bar, for 60 minutes

The greatest achievable pressure (140 bar) with 5% owf. of dye (sufficient) were selected as the dyeing conditions. These offered a high density in scCO$_2$, leading to a good solubility of dye molecules, and an adequate dyeing atmosphere in the system. This series of experiments were carried out at 140 bar, 5 % owf. of RD 1 and 60 minutes dyeing time, for the dry cotton fabric (Figure **4.7**A) and the wet cotton fabric (20 % owf. of water pre-treated) (Figure **4.7**B).

There was only a minor improvement in the f_k value and dye fixation after water pre-treatment. Compared with the dyed wool, the colour strength of both dyed dry cotton and wet cotton were low. The greatest value of $f_{k(dyed)}$ for both dry $[f_{k(dyed)} = 159.1]$ and wet $[f_{k(dyed)} = 191.3]$ cotton occurred when the temperature was 60 °C. The fixation value of both the dyed dry and the dyed wet cotton were noticeably lower than those of the dyed wool. The average fixation of dyed cotton was 20 %. Thus, no clear improvement in the dyeing of cotton was achieved by using water as the pre-treatment solvent and the co-solvent. The isocyanate group has high reactivity towards the primary hydroxyl groups of the cotton fabric. However, the dye molecule itself may be hindered from accessing the primary and secondary hydroxyl groups of the cotton fabric, due to the intra and inter molecular hydrogen bonds. The water pre-treatment was not effective for cotton dyeing in scCO$_2$. This may also be due to the remaining water being removed from the fabrics by scCO$_2$ itself, termed dehydration. Without the impact of plasticisation on cotton, cotton is consequently in the glassy state up to a relatively high temperature (around 220 °C), where the cotton is in a state which is hardly possible to dye [10]. Also, more reactive dyes would be hydrolysed if they were not reacted with the fabrics in a short time.

4.2.2.2 Investigation of the effect of the pressure on the dyeing of cotton, using RD 1 containing isocyanate reactive group

To investigate the effect of the pressure on the dyeing process, experiments were carried out at the optimum temperature, (see Section 4.2.2.1). In Figure **4.8**, the results are given for various pressures (from 80 to 140 bar) for the dyeing of both dry cotton and wet cotton (20 % owf. of water pre-treated for 30 minutes), with 4 % owf. of RD 1, at 60 °C for 60 minutes.

Figure **4.8** shows that the $f_{k(dyed)}$ value of both dyed dry and wet cotton increase consistently with pressure. Applying RD 1 on both dry cotton and wet cotton produced a low degree of fixation, (around 20 %) for pressure values from 80 bar to 140 bar. The greatest fixation occurred at 80 °C, as aforementioned, because only a small amount of dye molecules dissolved in $scCO_2$. There were only a small number of dye molecules that diffused into the cotton fabric, and almost all of the dye in the cotton fabric reacted with the hydroxyl groups in the cotton fabric. The great fixation occurring at the low pressures is due to few dye molecules being stripped off from the cotton fabric.

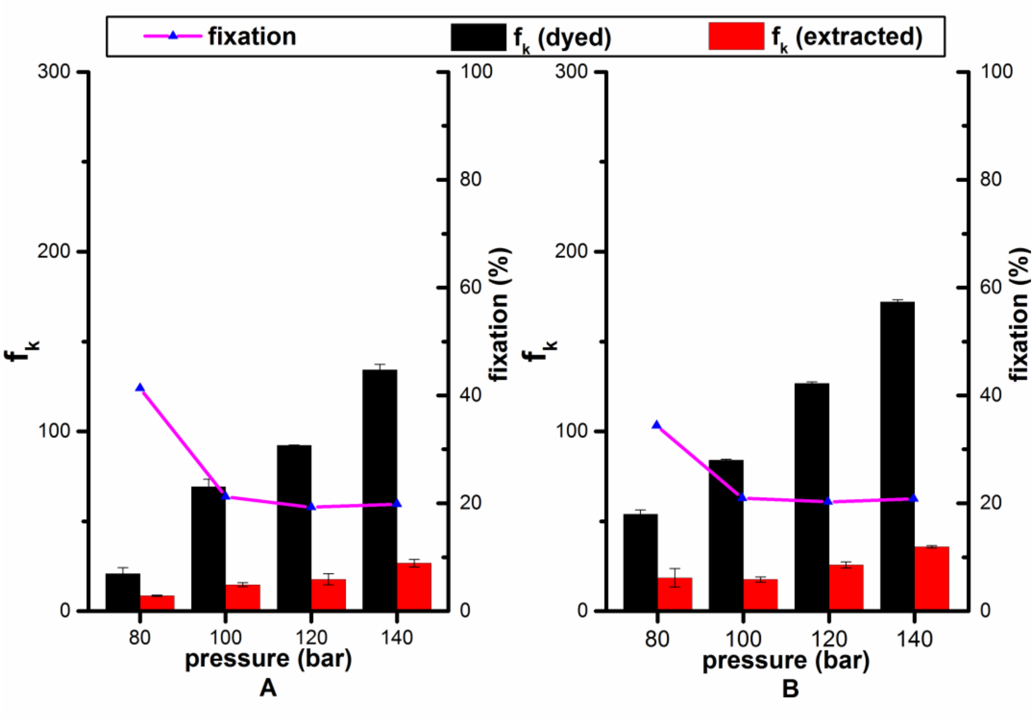


Figure 4.8 Effect of system pressure on the f_k value and the dye fixation of (A) dry cotton (B) wet cotton (20 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 4 % owf. of RD, at 60 °C 1, for 60 minutes

4.2.2.3 Investigation of the effect of dye loading on the dyeing of cotton, using RD 1 containing isocyanate reactive group

The dye loading test experiments were carried out under the chosen temperature and pressure conditions according to the previous investigations. The dyeing vessel loaded with 0.25 %, 0.5 %, 1 %, 2 %, 3 %, 4 %, 5 % owf. of RD 1 respectively, with the dyeing experiments being undertaken at 60 °C and 140 bar for 60 minutes. Dyeing results are depicted in Figure 4.9.

It can be seen from Figure 4.9, generally speaking, there was a significant increase in the $f_{k(dyed)}$ value when more dye was used. The fixation rate of RD 1 usually stabilised between 20 % to 30 %, the exception being the dyed dry cotton at 0.25 % owf. Relatively high fixation occurred when the dyed cotton did not have much colour. For the poorly dyed fabrics, the high fixation rate was explained in Sections 4.2.1.2, 4.2.1.3 and 4.2.2.2. The 20 % owf. of water pre-treatment gave only a small contribution to the increase in fixation. Even though the colour of the dyed cotton was stronger by using more dye, no significant reaction occurred between the dye and cotton. According to the fixation rate, most of the dye was only attached to the cotton via physical interactions and could be removed by acetone:water (1:1) easily.

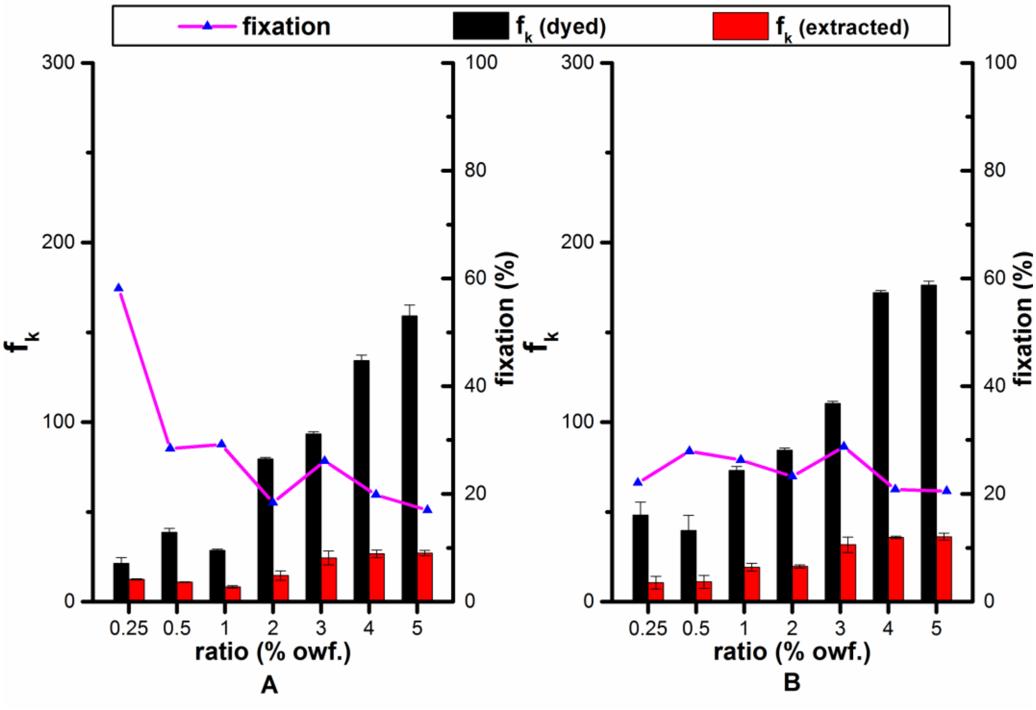


Figure 4.9 Effect of different loadings of RD 1 on the f_k value and the dye fixation of (A) dry cotton (B) wet cotton (20 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$, at 60 °C, 140 bar, for 60 minutes

4.2.2.4 Investigation of the effect of the amount of pre-treatment water on the dyeing of cotton, using RD 1 containing the isocyanate reactive group

As in Figure **4.7**, Figure **4.8** and Figure 4.9, it was shown that the use of 60 °C, 140 bar and a dye loading of 5 % owf. were appropriate dyeing conditions to achieve relatively effective cotton colouration. For this series of experiments, the same dyeing conditions were selected to establish the impact of different amounts of pre-treatment on cotton dyeing. From Figure 4.10 it is clear that cotton colouration was improved slightly from the $f_{k(dyed)}$ value of 159.1 to around 170.0 when the water pre-treatment method was applied. Consequently, the $f_{k(dyed)}$ value remained practically constant, showing a similar cotton colouration. There was no observable variation on the fixation before and after water pre-treatment. The fixation rate remained a low level around 20 %.

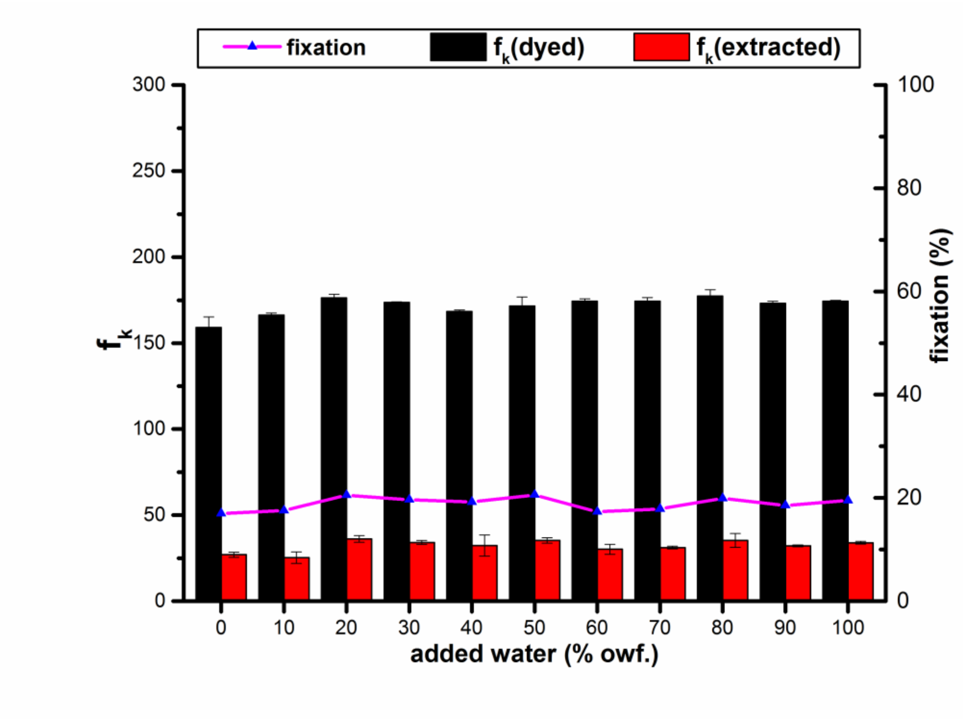


Figure 4.10 Effect of water addition in the pre-treatment process on the f_k value and the dye fixation of cotton dyed in scCO$_2$ with 5 % owf. of RD 1 at 60 °C, 140 bar, for 60 minutes

4.2.2.5 Investigation of the effect of dyeing time on the dyeing of cotton, using RD 1 containing the isocyanate reactive group

To investigate the effect of dyeing time on cotton dyeing, dyeing experiments were set up at 140 bar, 60 °C using 5 % owf. of RD 1, wet cotton, and cotton pre-treated with 20 % owf. of water for 30 minutes, for different dyeing times.

In Figure 4.11, the $f_{k(dyed)}$ value increased up to 124.756 in a very short period of time (30 minutes), showing relatively strong colouration. The consistent extent of cotton colouration indicates that dye diffusion into the cotton was established after roughly 60 minutes. The strongest colour [$f_{k(dyed)} = 199.7$] was obtained with the dyeing time of 180 minutes. Even though the colour of the dyed cotton increased initially, the fixation rate stayed at the same low level, (around 20.0 %) against increasing dyeing time. The exceptional fixation value (41.6 %) was found at 5 minutes.

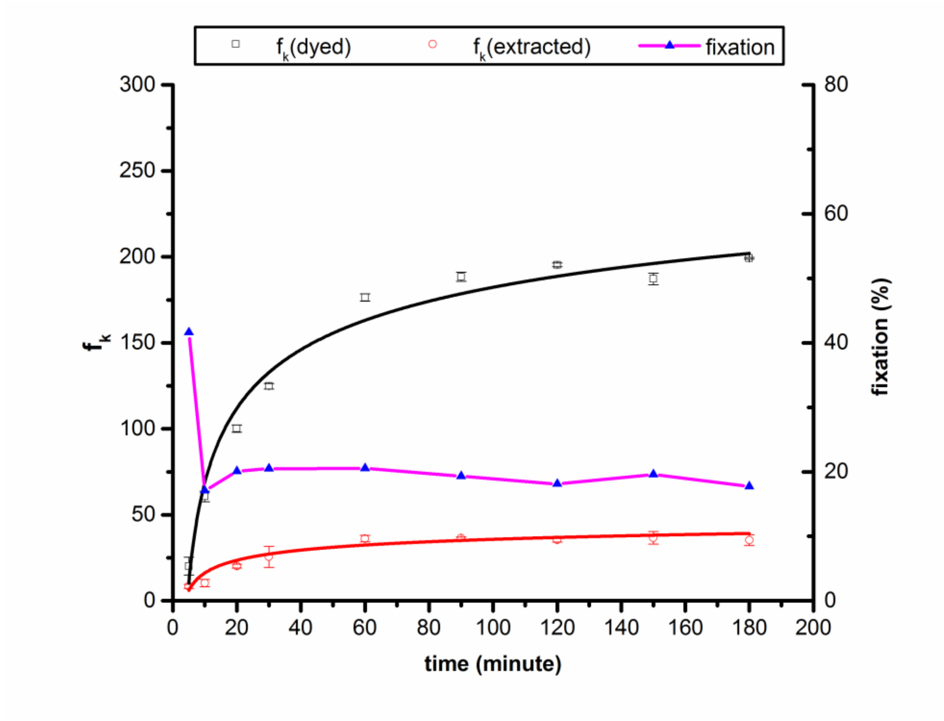


Figure 4.11 Effect of dyeing time on the f_k value and the dye fixation on wet cotton (20 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$ with 5 % owf. of RD 1, at 60 °C, 140 bar

4.2.2.6 Colour fastness testing

Table 4.2 The fastness of cotton fabrics, pre-treated to 20 % owf. of water, coloured with 5 % owf. of RD 1, in scCO$_2$ at 60 °C, 140 bar, at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	2	3-4	4	2	2	3	4
20	3	3-4	4	2	2	3	4
60	4	4	4	3	3	3	4
180	4	4	4	3	3	3	4

Table 4.2 shows some fading fastness for cotton that was dyed within 60 and 180 minutes. The longer dyeing time gave better wash fastness in both fading and staining. In general, the wash fastness of the dyed cotton was worse than the dyed wool, but a much stronger colour on the washed cotton was seen, when compared to the dyed cotton stripped (extracted) by acetone:water (1:1).

To show the colour difference of washed cotton and the extracted equivalence, the f_k values and fixation rates are shown in Table 4.3. This relates to the colour of dyed cotton $f_{k(\mathrm{dyed})}$, the colour of cotton after extracted by acetone:water (1:1) $f_{k(\mathrm{extracted})}$, the colour of cotton that was washed with water and detergent $f_{k(\mathrm{washed})}$, the fixation based on the $f_{k(\mathrm{extracted})}$ value Fixation (extracted) and the fixation based on the $f_{k(\mathrm{washed})}$ value Fixation (washed). The colour and fixation of the washed cotton were more than three times those of the cotton stripped by acetone. After wash testing, the fixation reached 76.1 % after 180 minutes of dyeing. Thus, the dyed cotton has the potential to be used in some commercial applications due to the good wash fastness. Even though there is no sufficient chemical reaction between the cotton fibre and the dye, the physical attachment is strong to avoid colour fading when being washed.

Table 4.3 f_k values of dyed cotton, of extracted cotton and of washed cotton fabrics, and fixation rate, using RD 1 in scCO$_2$, for different dyeing times

Dyeing time (minute)	$f_{k(\mathrm{dyed})}$	$f_{k(\mathrm{extracted})}$	$f_{k(\mathrm{washed})}$	Fixation (extracted)	Fixation (washed)
10	60.6	10.4	38.2	17.1 %	62.9 %
20	100.2	20.1	61.8	20.1 %	61.7 %
60	176.3	36.5	133.2	20.5 %	75.6 %
180	199.2	35.6	151.6	17.7 %	76.1 %

4.2.3 Microscopy study of dyed wool and cotton dyed with RD 1 in scCO$_2$

4.2.3.1 SEM analysis

To gain a better understanding of the effect of the scCO$_2$ dyeing process on the surface of dyed cotton fibres and dyed wool fibres, a microscopy study was carried out using scanning electron microscopy (SEM). Figure 4.12 shows SEM images of the surface of the untreated fibres, of the scCO$_2$/H$_2$O treated fibres and of the fibres dyed in scCO$_2$/H$_2$O.

Figure **4.12**a demonstrated that untreated, as supplied cotton fibres were relatively smooth, there being some wrinkles on the surface. Figure **4.12**b shows the image of the cotton fibres that were treated with $scCO_2/H_2O$ under the described dyeing conditions without any dye present. Many deep and pleat-like wrinkles appear on the surface of the fibre. These wrinkles were assumed to be damage because of the depressurisation steps of the supercritical dyeing process when water was present in the cotton [11]. Particles on the cotton fibre surfaces appeared after the dye uptake in $scCO_2/H_2O$, as depicted in Figure **4.12**e. Fibrillation and deep wrinkles were observed on the surface of the dyed cotton fibres as well. The slight damage, especially the fibrillation, on the surface of the fibre might have been caused by the reaction between RD 1 and the cotton fibre.

Figure **4.12**b shows the SEM image of the untreated wool showing a smooth and intact surface. There were some fragments of the wool scale on the wool fibre surfaces after the treatment with water and then subsequently $scCO_2$, without dye being present (Figure **4.12**d). In Figure **4.12**f, apart from some particles being seen, no fibrillation was observed on the surface of the dyed wool fibres. Thus, the reported process did not seriously damage the wool fibre surface. Particles found on the surface of the dyed fibres were likely to be present as a result of oligomer [12].

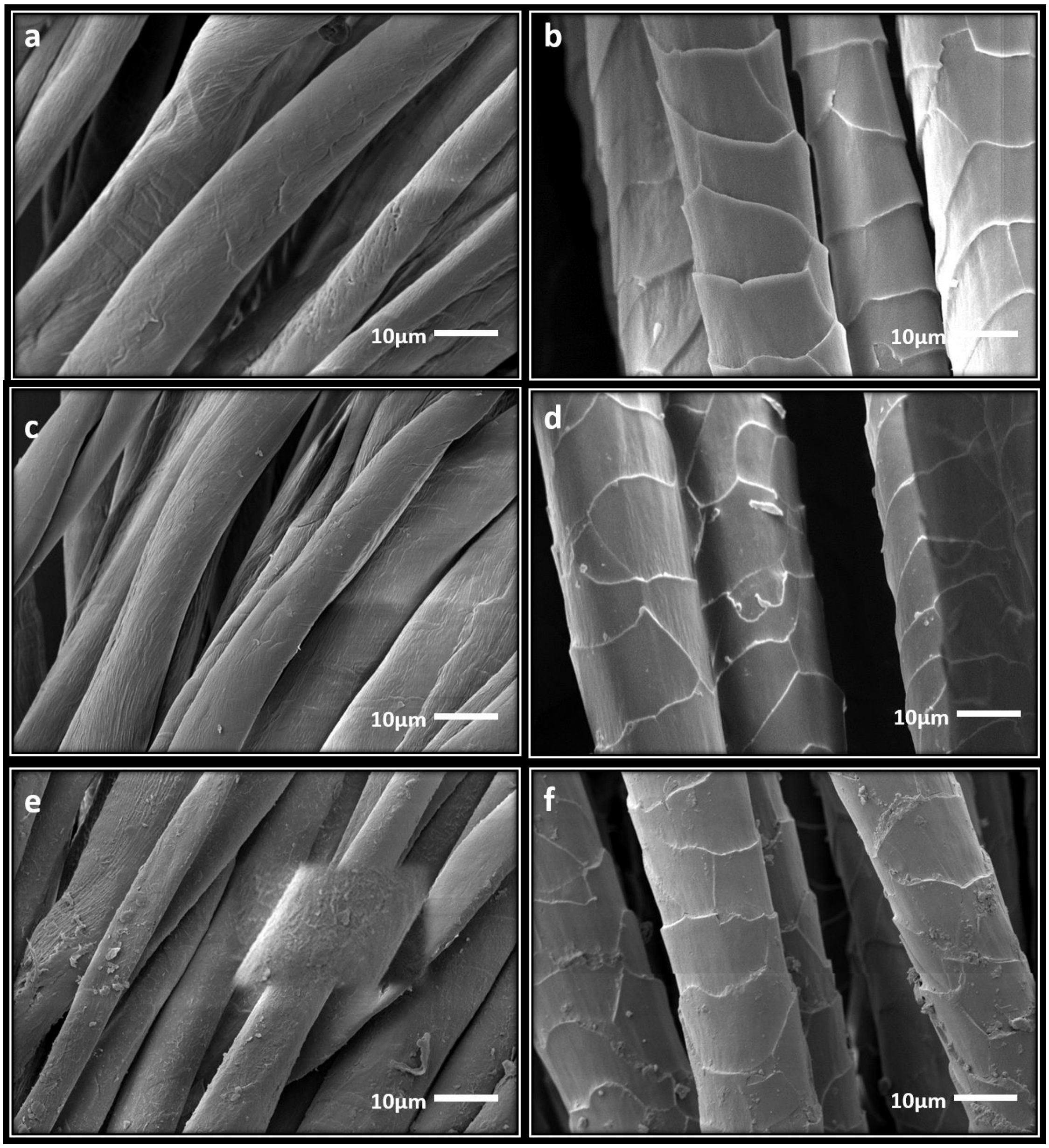


Figure 4.12 SEM images of the surface of (a) supplied cotton fibres; (b) supplied wool fibres; (c) cotton fibres pre-treated with 20 % owf. of water, treated at 60 °C, 140 bar for 180 minutes in $scCO_2$; (d) wool fibres pre-treated with 50 % owf. of water, treated at 70 °C in $scCO_2$, 140 bar for 180 minutes; (e) cotton fibres pre-treated with 20 % owf. of water, coloured with 5 % owf. of RD 1, in $scCO_2$ at 60 °C, 140 bar, for 180 minutes; (f) wool fabric pre-treated with 50 % owf. of water, coloured with 5 % owf. of RD 1, in $scCO_2$ at 70 °C, 140 bar for 180 minutes.

4.2.3.2 Cross-section studies

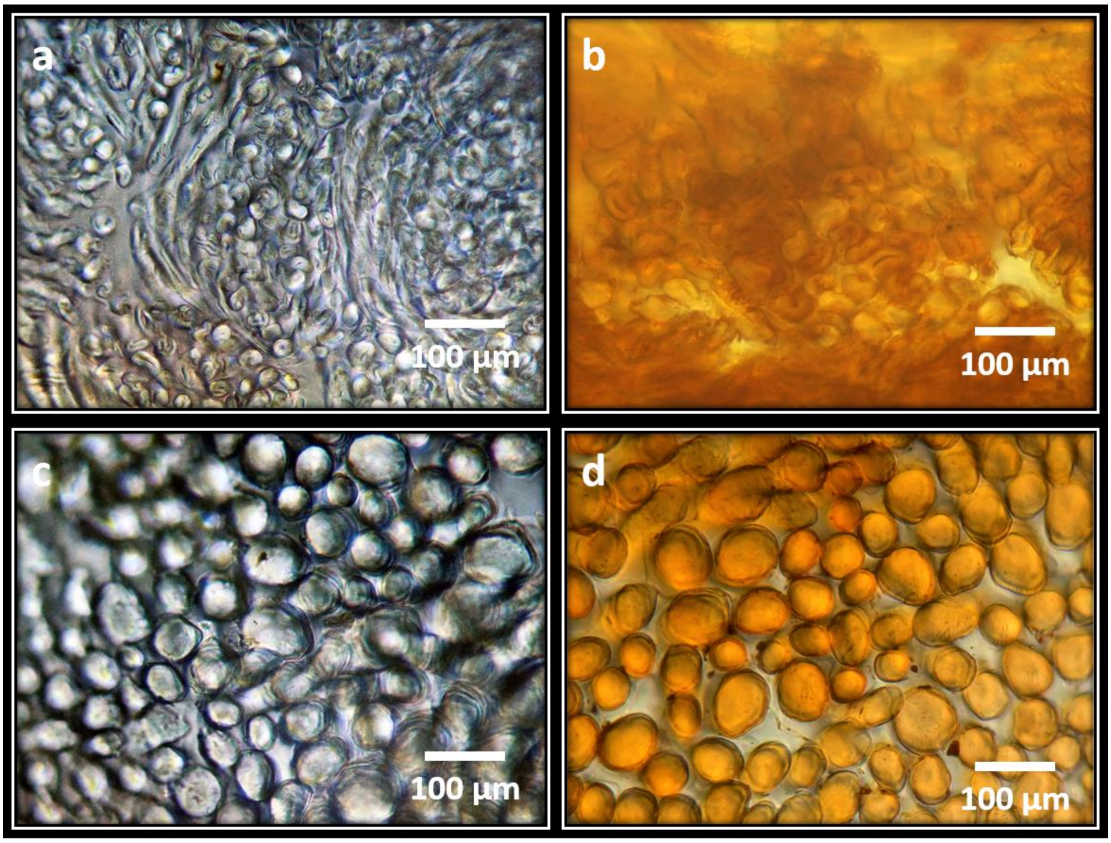


Figure 4.13 Cross-section images of (a) supplied cotton fabric; (b) cotton fabric pre-treated with 20 % owf. of water, coloured with 5 % owf. of RD 1, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (c) supplied cotton fabric (d) woo fabric pre-treated with 50 % owf. of water, coloured with 5 % owf. of RD 1, in $scCO_2$ at 70 °C, 140 bar, for 180 minutes. (x62.5)

The cross-section images of untreated, as supplied cotton untreated, as supplied wool; dyed cotton and dyed wool are presented in Figure 4.13.

Ring dyeing was found in the cotton dyed using RD 1 supercritical dyeing, depicted in Figure 4.12b. The colouration was inconsistent. The dyeing of the cotton in $scCO_2/H_2O$ was not even. The penetration of $scCO_2$ mixed with water was not good.

Figure 4.13d shows a cross-section photograph of the wool fabrics dyed under the stated conditions. Good dye uptake occurred after dyeing in $scCO_2$. It can be seen that individual wool fibres were well penetrated by the RD 1 molecules.

4.2.4 Dyeing natural fabrics using C.I. Disperse Orange 3 in the supercritical dyeing system

Traditional disperse dyes have been used for the supercritical dyeing of natural fabrics [13]. The dyeing qualities of dyed fibre based natural fabrics, using the traditional disperse dyes in $scCO_2$ are not good enough to meet commercial requirement [12-15]. In order to assess the advantages of incorporating the isocyanate reactive group in a disperse dye, experiments using unmodified C.I. Disperse Orange 3 were conducted under the same dyeing conditions as a comparison.

In the studies described in Sections 4.2.1.2 and 4.2.2.2., attention was given to the use of higher pressures to provide a greater density of $scCO_2$, leading to the greater solubility of the dye in $scCO_2$. The adequate dye loading can help to improve the dyeing qualities caused by insufficient dye. Thus, to obtain the optimum dyed fabrics in $scCO_2$ using C.I. Disperse Orange 3, 5 % owf. of dye, 140 bar and 180 minutes of dyeing time were chosen. However, the amount of water in the pre-treatment needed to be considered, as the water plays an important role in the supercritical dyeing of natural fabrics. Also, the appropriate dyeing temperature in $scCO_2$ using C.I. Disperse Orange 3 needed to be established. Use of a low temperature provided a greater density of the $scCO_2$, which should have a relatively low diffusivity and high viscosity. High temperature would bring a good diffusion rate of the dye in $scCO_2$ [16]. The density of the $scCO_2$ would decreased with the increasing temperature, leading to poor solubility of the dye in the $scCO_2$ [17].

4.2.4.1 Wool dyeing using C.I. Disperse Orange 3 in $scCO_2$

Fabrics were dyed using 5 % owf. of C.I. Disperse Orange 3, with different amounts of water in the pre-treatment process, at 70 °C, 140 bar, for 180 minutes. Figure 4.14 shows that under these conditions, the most appropriate water addition in the dyeing and pre-treatment process for the dyeing of wool was obtained at 40 % owf.

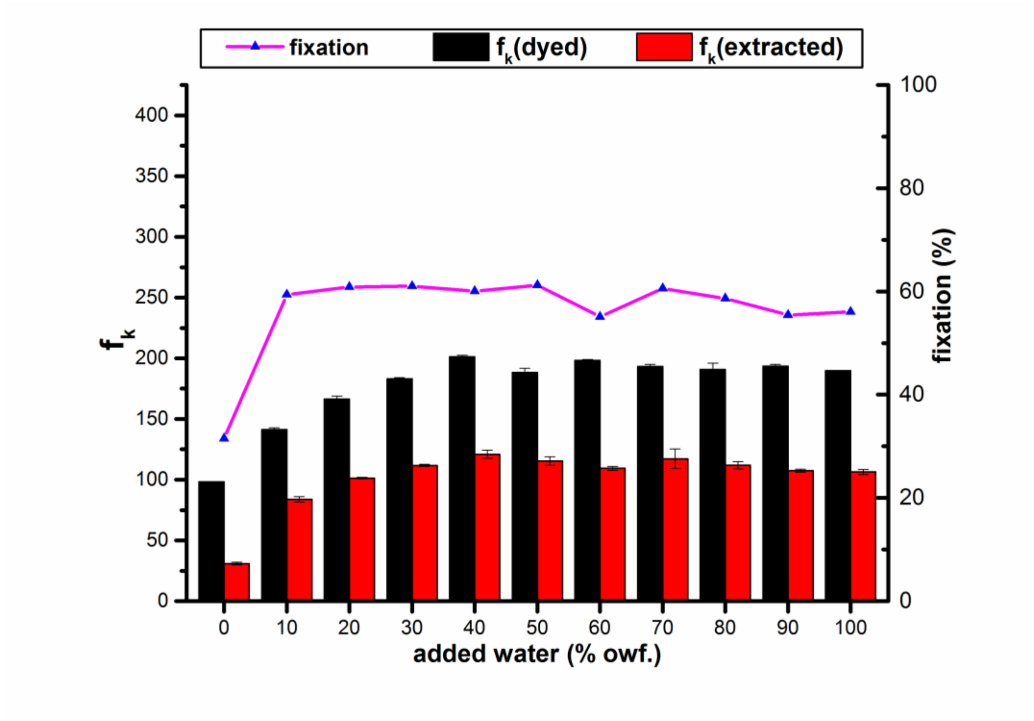


Figure 4.14 Effect of water addition in the pre-treatment process on the f_k value and on the dye fixation of the wool, dyed in scCO$_2$ with 5 % owf. of C.I. Disperse Orange 3 at 70 °C, 140 bar, for 180 minutes

Then, the dyeing experiments were carried out using 40 % owf. water addition in the pre-treatment process and 5 % owf. of C.I. Disperse Orange 3, at 140 bar for 180 minutes dyeing time (Figure 4.15). The greatest colouration was obtained at 90 °C. However, the optimum conditions for wool dyeing using C.I. Disperse Orange 3 were observed at the dyeing conditions of 5 % owf. of dye, 40 % owf. of water pre-treatment, 70 °C, 140 bar and 180 minutes dyeing time, considered from both economical and efficiency viewpoints.

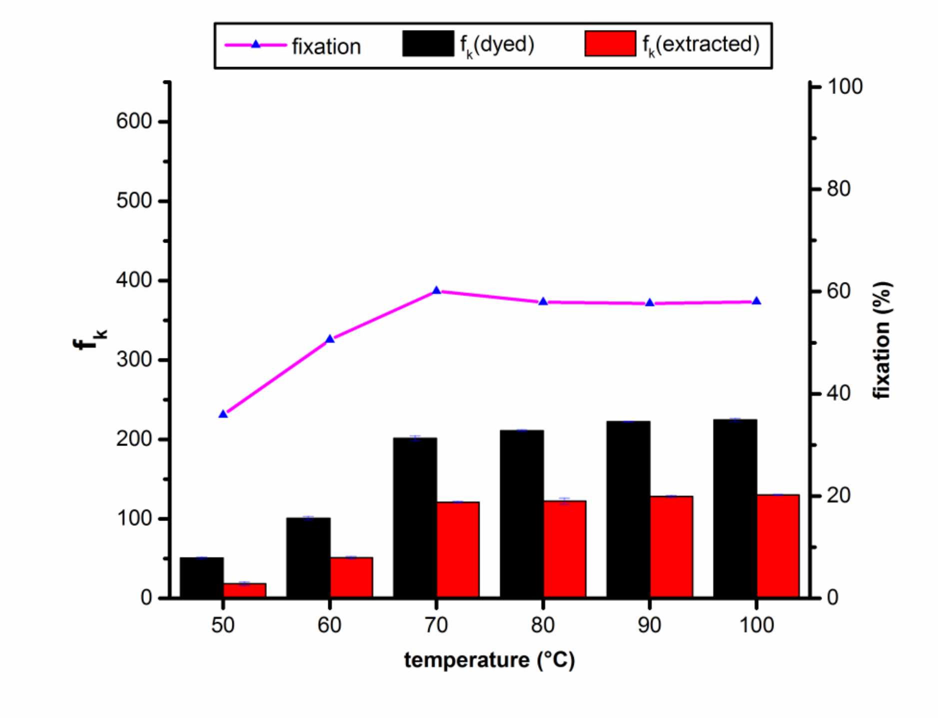


Figure 4.15 Effect of the system temperature of the f_k value and on the dye fixation of wool (40 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of C.I. Disperse Orange 3, at 140 bar, for 180 minutes

4.2.4.2 Cotton dyeing using C.I. Disperse Orange 3 in $scCO_2$

A series of experiments for the dyeing of cotton in $scCO_2$ was carried out using different amounts of water for the pre-treatment process, with 5 % owf. of C.I. Disperse Orange 3, at 60 °C, 140 bar, for 180 minutes. Figure 4.16 shows the minor improvement on the $f_{k(dyed)}$ value that was observed after 10 % owf. of water was added during the pre-treatment. The $f_{k(dyed)}$ value remained stable even when more water was used. A 12.5 % variations in the fixation rate when the addition of water ranged from 0 % owf. to 100 % owf..

An investigation into the effect of temperature on the $scCO_2$ dyeing was carried out at different dyeing temperatures using 5 % owf. of C.I. Disperse Orange 3, with 10 % owf. of water being used in the pre-treatment and dyeing system, at 140 bar, for 180 minutes. Figure 4.17 shows that poor colouration was observed until the temperature was increased to 70 °C. The $f_{k(dyed)}$ value stabilised at around

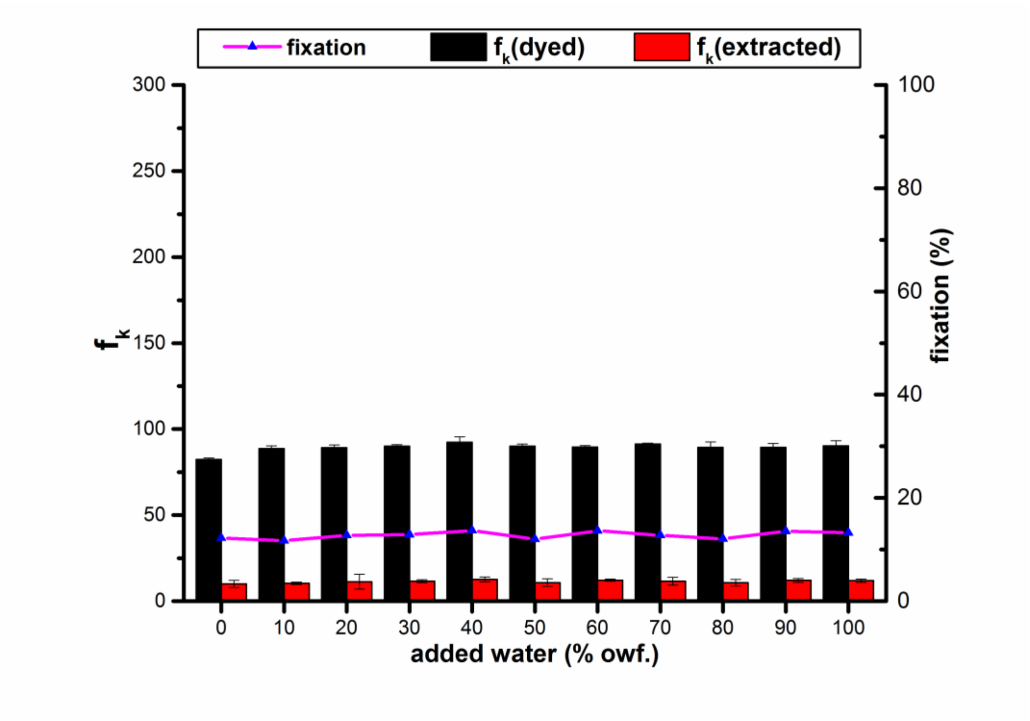


Figure 4.16 Effect of water used in the pre-treatment process, on the f_k value and on the dye fixation in cotton dyed in scCO$_2$ using 5 % owf. of C.I. Disperse Orange 3, at 60 °C, 140 bar, for 180 minutes

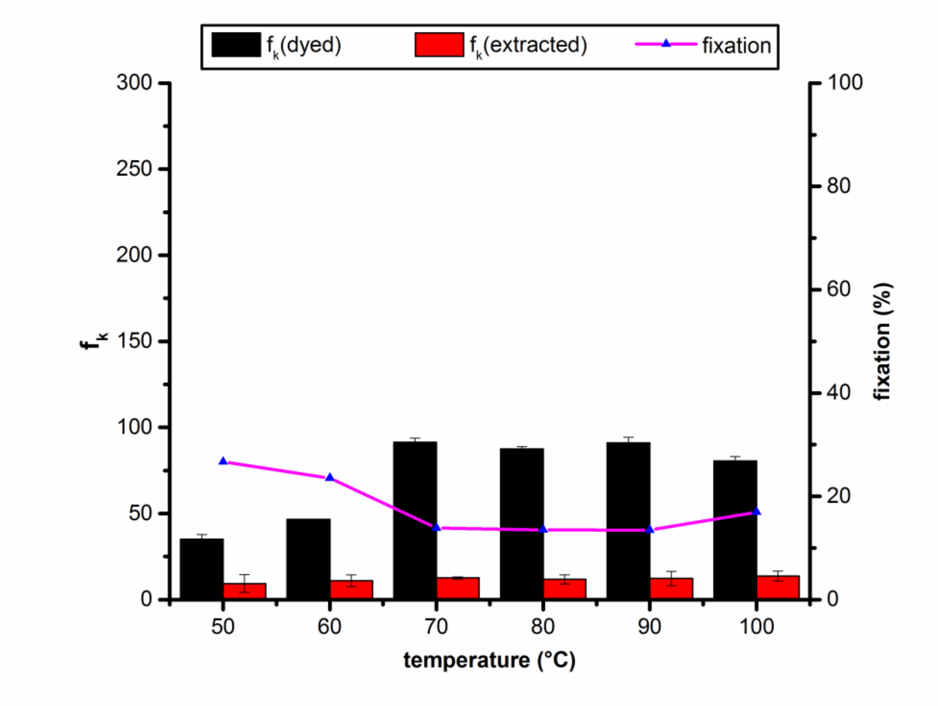


Figure 4.17 Effect of temperature on the f_k value and on the dye fixation on cotton (10 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$ with 5 % owf. of C.I. Disperse Orange 3 at, 140 bar, for 180 minutes

80, from 70 °C to 100 °C. Unsurprisingly, the fixation rate was very poor when the C.I. Disperse Orange 3 was used in the supercritical dyeing.

The best dyeing results when using C.I. Disperse Orange 3 in $scCO_2$ were obtained with 5 % owf. of dye, with 10 % owf. of water in the pre-treatment and dyeing system, at 70 °C and 140 bar for 180 minutes.

4.2.5 Comparison of the dyeing results for the C.I. Disperse Orange 3 and for RD 1 in supercritical dyeing

4.2.5.1 Description of dyed samples and visual assessments

Figure 4.18 presents relevant dyed samples.

Fabric samples A, B, C, D, E and F were dyed with RD 1. 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.

Fabric samples G, H, I, J, K and L were dyed with C.I. Disperse Orange 3. G: dyed wool sample; H: dyed wool sample extracted with acetone:water (1:1); I: dyed wool sample washed with water; J: dyed cotton sample; K: dyed cotton sample extracted with acetone:water (1:1); L: dyed cotton sample washed with water and detergent.

The dyeing conditions were: Wool sample A - 70 °C, 140 bar, 5 % owf. of RD 1, 50 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time; cotton sample D - 60 °C, 140 bar, 5 % owf. of RD 1, 20 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time; wool sample G - 70 °C, 140 bar, 5 % owf. of C.I. Disperse Orange 3, 40 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time, cotton sample J - 70 °C, 140 bar, 5 % owf. of C.I. Disperse Orange 3, 10 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time.

Wool sample A, dyed with RD 1 had a strong orange colouration. The colour difference amongst dyed wool A, the extracted wool B and the washed wool

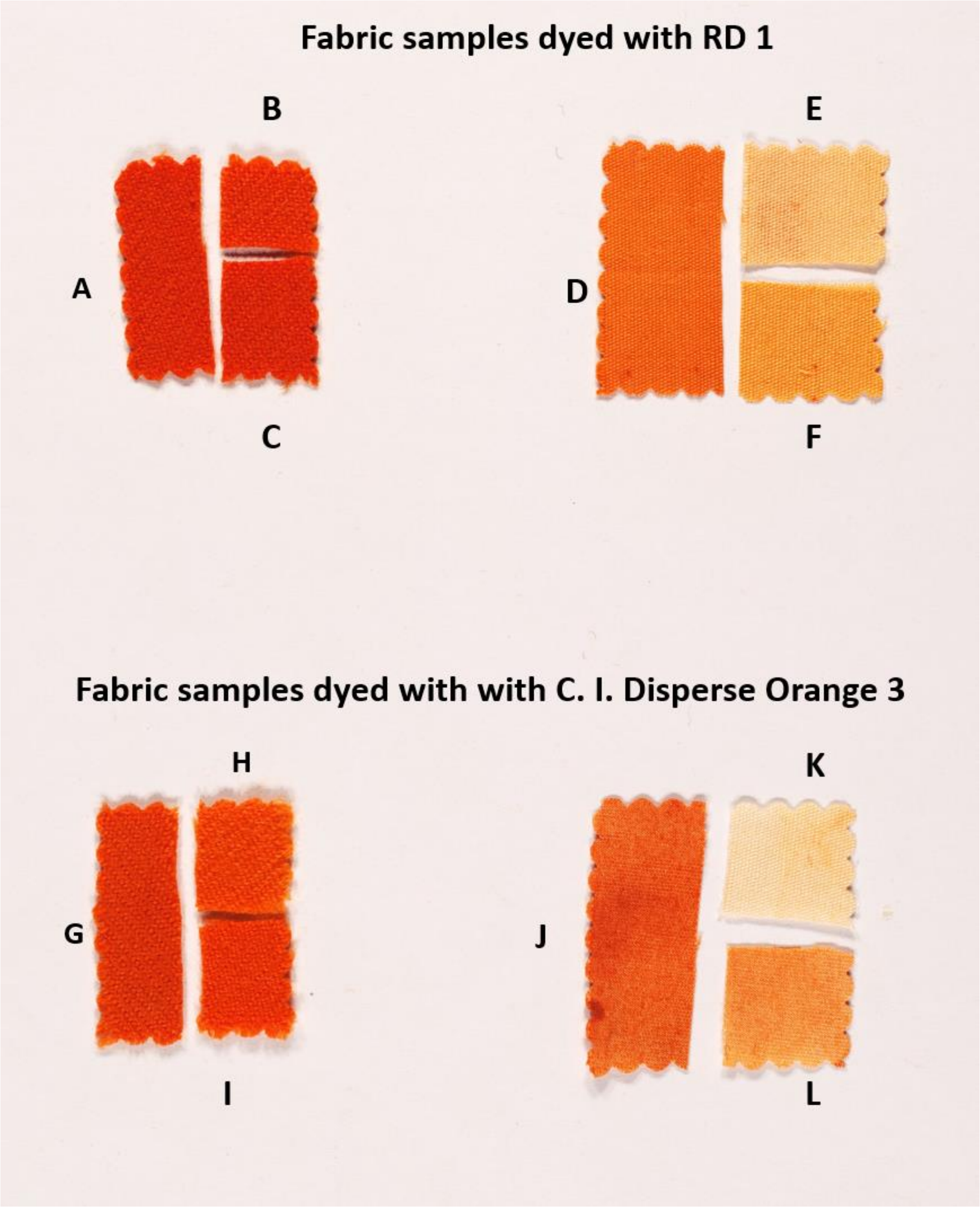


Figure 4.18 Dyed wool and cotton samples using RD 1 and C.I. Disperse Orange 3 in $scCO_2$

C was small. Thus, commercially acceptable dyeing was observed on the dyed wool sample (Figure 4.18).

The dyed cotton sample D was a lighter orange colour than dyed wool A using RD 1. Most of the dye was removed after extraction by acetone:water (1:1) (Figure 4.18 E). Moreover, colour was lost in washing (Figure 4.18 F), but not as much as the colour lost by extraction (Figure 4.18 E). A satisfactory levelling property of the cotton sample D dyed with RD 1 was achieved.

Wool sample G dyed with C.I. Disperse Orange 3 was strongly coloured but was slightly less coloured than the wool sample A dyed by RD 1. Colour fading occurred on stripping and washing (Figure 4.18 H and I). The levelness of the dyed wool G was excellent.

Cotton sample J, dyed with C.I. Disperse Orange 3 was relatively strongly coloured in the middle, but less coloured at the edge. A very pale yellow colour was observed with cotton sample K after the extraction. Some orange colourant still remained on the washed cotton sample L due to the van der Waals force between the cotton and the dye. The levelness of the dyed cotton H was very poor.

4.2.5.2 Colour [$f_{k(dyed)}$ value, fixation rate and CIE L*a*b* value] of RD 1 and C.I. Disperse Orange 3 on wool fabrics and on cotton fabrics

Table 4.4 The $f_{k(dyed)}$ value and the fixation rate of dyed wool fabrics and of cotton fabrics using RD 1 and C.I. Disperse Orange 3 respectively under their chosen dyeing conditions in scCO$_2$, for 180 minutes

	Wool		**Cotton**	
	$f_{k(dyed)}$	**Fixation**	$f_{k(dyed)}$	**Fixation**
C.I. Disperse Orange 3	201.4 (Figure 4.18 G)	60.1 % (Figure 4.18 G)	91.4 (Figure 4.18 J)	13.8 % (Figure 4.18 J)
RD 1	400.9 (Figure 4.18 A)	92.7 % (Figure 4.18 A)	199.2 (Figure 4.18 D)	17.7 % (Figure 4.18 D)

The results shown in Table 4.4 show that great improvements in both the colour strength and the fixation rate were achieved by introducing the isocyanate group to the C.I. Disperse Orange 3, for wool dyeing in scCO$_2$. With the addition of the isocyanate group, the colouration on the wool fabric was increased from the $f_{k(dyed)}$ of 201.4 to 400.9. Also, there was a 30 % increase on the fixation rate. For cotton dyeing, the $f_{k(dyed)}$ value was more than doubled when the C.I. Disperse Orange 3 was replaced by the RD 1. However, the low fixation rate of the dyed cotton fabrics using either C.I. Disperse Orange 3 or RD 1 presents a great obstacle for cotton dyeing in $scCO_2$.

Table 4.5 CIE $L^*a^*b^*$ value of dyed wool fabric using 50 % owf. of water, pre-treated and 5 % owf. of dye at 70 °C, 140 bar in 180 minutes in $scCO_2$; cotton fabric dyed using 20 % owf. of water, pre-treated and 5 % owf. of dye at 60 °C, 140 bar, for 180 minutes in $scCO_2$

Sample	L^*	a^*	b^*
Wool (Figure 4.18 A)	40.96	46.94	42.86
Cotton (Figure 4.18 D)	51.74	39.28	44.97

Table 4.5 shows that similar colour characteristics in the orange hue, such as the colour lightness (L^*), colour-opponent dimension values of a^* and b^* in the CIE 1976 (L^*, a^*, b^*) colour space model, were observed for the dyed wool and cotton fabric.

4.3 Conclusions

The concept of using a reactive, isocyanate-group modified dye to dye natural fabrics has been introduced into the supercritical dyeing. Experiments were carried out under different dyeing conditions, revealing that it is possible to dye wool and cotton fabrics with the isocyanate disperse dye under relatively mild conditions in $scCO_2$ in presence of small amount of water, in 30 minutes.

Strong colouration was obtained at greater pressures of $scCO_2$, due to the higher solubility of the dye in $scCO_2/H_2O$. Use of a higher temperature improves the mobility, diffusivity and potentially enhances the reactivity of the dye, but also decreases the solubility of dye at constant pressure. Moreover, water has a strong effect on the wool dyeing because it acts as a swelling agent and increases the density of the $scCO_2$. It was found that dyeing with 5 % owf. of dye and 50 % owf. of water at 70 °C, 140 bar for 180 minutes gave the greatest $f_{k(dyed)}$ value (373.6).

The fixation rate increased with time up to 60 minutes, reaching 98.9 %. Good wash fastness results were obtained. Staining fastness data were all good and the fading fastness improved with longer dyeing times. No clear damage to the wool was observed by SEM analysis. The cross section analysis that showed the wool fibres were well penetrated by the RD 1.

The dyeing quality of the dyed cotton need to be further improved. Even though water pre-treatment helped increase the $f_{k(dyed)}$ value slightly, the highest $f_{k(dyed)}$ value was only 199.2 obtained using 60 °C, 140 bar, by the 20 % owf. of water pre-treatment with 5 % owf. of dye stuff and the dyeing time of 180 minutes. The dyed cotton had acceptable colouration but the fixation rate was very poor. There was little difference in the unsatisfactory fixation (around 20 %) by changing pressure, temperature, the amount of water for pre-treatment or dyeing time. Ring dyeing was observed in the microscopy study. The low fixation and ring dyeing indicated that the dye did not penetrate into, or chemically bond to, the cotton fibre. The main obstacle of dyeing cotton might be that the cotton fabric cannot be swollen properly in the mixed supercritical and water fluid. Consequently, it was not easy for the reactive disperse dye to access the mobile phase in the cotton. The insufficient contact between the cotton, the $scCO_2$ and the dye led to the side reaction between the reactive disperse dye and water occurring. The wash fastness of the dyed cotton fabrics was acceptable. The physical adsorption between the dye and the cotton fabric provided a high fixation rate of up to 76.1 % when the stripping (extraction) was replaced by washing.

For comparison, C.I. Disperse Orange 3 was used in the supercritical dyeing. In wool dyeing, the relatively weak colouration and a poor fixation rate was obtained contrasting with the excellent dyeing results using RD 1. The results from the dyeing of cotton using C.I. Disperse Orange 3 were unsatisfactory, as seen in the colour depth, the fixation and the levelness. However, the fixation on cotton using the RD 1 was also not good, the introduction of isocyanate group on the disperse dye changed the solubility of the dye in $scCO_2$ leading to better level dyeing for cotton.

The isocyanate-group containing reactive disperse dye could be a satisfactory dye for supercritical wool dyeing indicating that there may be potential for introducing the isocyanate into other chromophoric group.

4.4 References

1. Purnell, C.J. and R.F. Walker, *Methods for the determination of atmospheric organic isocyanates. A review.* Analyst, 1985. **110**(8): p. 893-905.
2. Lin, N., J. Huang, P.R. Chang, D.P. Anderson, and J. Yu, *Preparation, modification, and application of starch nanocrystals in nanomaterials: a review.* Journal of nanomaterials, 2011. **2011**: p. 20.
3. Li, X., L.G. Tabil, and S. Panigrahi, *Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review.* Journal of Polymers and the Environment, 2007. **15**(1): p. 25-33.
4. George, J., M. Sreekala, and S. Thomas, *A review on interface modification and characterization of natural fiber reinforced plastic composites.* Polymer Engineering & Science, 2001. **41**(9): p. 1471-1485.
5. Chao, T.-Y., H.-L. Chang, W.-C. Su, J.-Y. Wu, and R.-J. Jeng, *Nonlinear optical polyimide/montmorillonite nanocomposites consisting of azobenzene dyes.* Dyes and Pigments, 2008. **77**(3): p. 515-524.
6. Yamawaki, K., *Isocyanate group-containing reactive azo compounds, their preparation, and their reaction products*. 2008, Toppan Printing Co., Ltd., Japan . p. 14pp.
7. Six, C. and F. Richter, *Isocyanates, organic.* Ullmann's Encyclopedia of Industrial Chemistry, 2003.
8. Özcan, A.S., A.A. Clifford, K.D. Bartle, and D.M. Lewis, *Solubility of disperse dyes in supercritical carbon dioxide.* Journal of Chemical & Engineering Data, 1997. **42**(3): p. 590-592.
9. ISO, Textiles-Tests for colour fastness-Colour fastness to domestic and commercial laundering, British Standards Institution (BSI Group), London, UK, 2010.
10. Beltrame, P.L., A. Castelli, E. Selli, A. Mossa, G. Testa, A.M. Bonfatti, and A. Seves, *Dyeing of cotton in supercritical carbon dioxide.* Dyes and Pigments, 1998. **39**(4): p. 335-340.
11. Katayama, S., L. Zhao, S. Yonezawa, and Y. Iwai, *Modification of the surface of cotton with supercritical carbon dioxide and water to support nanoparticles.* The Journal of Supercritical Fluids, 2012. **61**: p. 199-205.
12. Banchero, M., *Supercritical fluid dyeing of synthetic and natural textiles - a review.* Coloration Technology, 2013. **129**(1): p. 2-17.
13. Gebert, B., W. Saus, D. Knittel, H.-J. Buschmann, and E. Schollmeyer, *Dyeing natural fibers with disperse dyes in supercritical carbon dioxide.* Textile Research Journal, 1994. **64**(7): p. 371-374.
14. Özcan, A., A. Clifford, K. Bartle, P. Broadbent, and D. Lewis, *Dyeing of modified cotton fibres with disperse dyes from supercritical carbon dioxide.* Journal of the Society of Dyers and Colourists, 1998. **114**(5-6): p. 169-173.
15. Bach, E., E. Cleve, and E. Schollmeyer, *Past, present and future of supercritical fluid dyeing technology–an overview.* Review of Progress in Coloration and Related Topics, 2002. **32**(1): p. 88-102.
16. Debenedetti, P.G. and R. Reid, *Diffusion and mass transfer in supercritical fluids.* AIChE journal, 1986. **32**(12): p. 2034-2046.
17. Jessop, P.G. and W. Leitner, *Chemical synthesis using supercritical fluids*. 2008: John Wiley & Sons.

Chapter 5 Dyeing natural fabrics with highly soluble reactive disperse dyes

5.1 Introduction

5.1.1 Background

The general method of designing reactive disperse dye structures involves modifying traditional disperse dye molecules with reactive groups that was then able to form a covalent bond with fibres of natural textile. The dyes are typically based on the azo-benzyl chromophore or the anthroquinonyl chromophore due to their strong colour strength and versatility when modifying their solubilising power and their reactive functionality [1]. Initially, the most common reactive functional group used in reactive dyes for dyeing natural fibres was the triazine group. This led to a range of further reactive groups being developed, including the dichlorotriazinyl, trichloropyrimidyl, vinylsulphonyl, dichloroquinoxalinyl and difluorochloropyrimidyl groups [2]. To increase the fixation of dye molecules onto textile fibres, bifunctional reactive dyes have also been developed [3]. These fall into the categories of homobifunctional molecules and heterobifunctional molecules, whereby the dye structure can contain the same functional (reactive) group at two positions within the molecule or two different functionalities at two different positions, respectively [3]. However, an increase in such functionality can often lead to an increase in polarity. This, in turn, leads to decreased solubility in $scCO_2$. Thus, a compromise is often required to provide both effective solubility and substrate fixation [4].

The solubility of dyes in $scCO_2$ has played a significant role in the supercritical dyeing process [5]. Dye solubility can be easily adjusted by optimising the processing temperature and pressure. To obtain high quality dyeing at a low cost, the solubility in $scCO_2$ should be sufficient for conditions to be maintained in commercial dyeing machinery [6]. Modifying dye structures to increase solubility in $scCO_2$ was the main challenge of this study. Alkyl chains can increase the solubility of dye molecules in $scCO_2$ and also increase the van der Waals interactions between natural fabrics and dyes [7].

In this study, the isocyanate functionality (Chapter 4) was used as the reactive group. Alkyl solubilising groups of different lengths have great potential to increase the solubility of the dyes in supercritical or near $scCO_2$. Excellent dyeing results can be obtained following the pre-treatment of the substrate with one or more hydrogen bond acceptors, such as water. The solubility of the synthesised dyes in $scCO_2$ is very important parameter in this study, which was to be investigated in this study. However, because of the limitation of the facilities, the solubility of those dyes in the $scCO_2$ was not established.

Effective fixation of the dyes combined with relatively fast reaction rates were features of the evaluated dyeing method that provides good wash fastness and light fastness. The most commercially valuable advantage of this method is that the dyeing process can be carried out under relatively mild dyeing conditions within 20 minutes, preferably at 70 °C and 140 bar.

5.1.2 Rationale

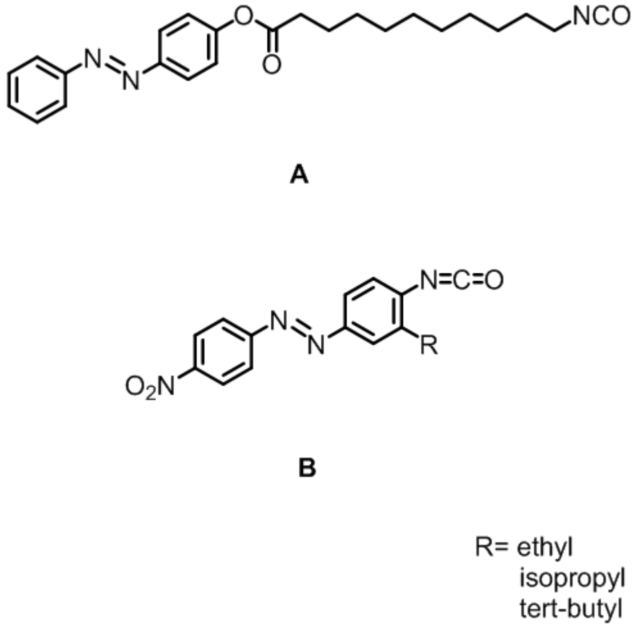


Figure 5.1 Two designed structures

Two different dyes containing both alkyl groups and isocyanate group were used for the supercritical dyeing of natural fabrics. Structures of these dyes are presented in Figure 5.1.

The structure (A), possessing a long alkyl group ending with an isocyanate group, has 11 extra carbon atoms that would reduce the chromophoric strength per unit mass of the chromophore molecule. The introduction of the long alkyl group led to an increase of 72 % molecular weight of the original structure. The extra aliphatic characters should increase the solubility of the dye in $scCO_2$ and have the effect of reducing the intensity of colour per unit mass of colourant. However these aliphatic chains would reduce the affinity of the dyes to polar natural fabrics.

The structure (B) was synthesised from 4-nitro-benzeneamine. Two steps were needed to obtain the final product without any further purification due to the high purity of the product formed (characterisation is presented in Chapter 7). The starting materials are also cheap and easy to source. The most important advantage compared to the use of structure (A) is that the additional, small alkyl groups have great potential to increase the solubility of the dye in $scCO_2$ [8, 9], but would not lose too much colour of the chromophore group.

Thus, structure (B) was selected as the target molecule. The main objective of this work was to establish the way the different alkyl group impacted on the dyeing results.

Synthetic route to these dyes RD 2, RD 3 and RD 4 is shown in Figure 5.2. In order to assess the impact of the introduced alkyl groups on the supercritical dyeing process and on textile colouration, these dyes were prepared.

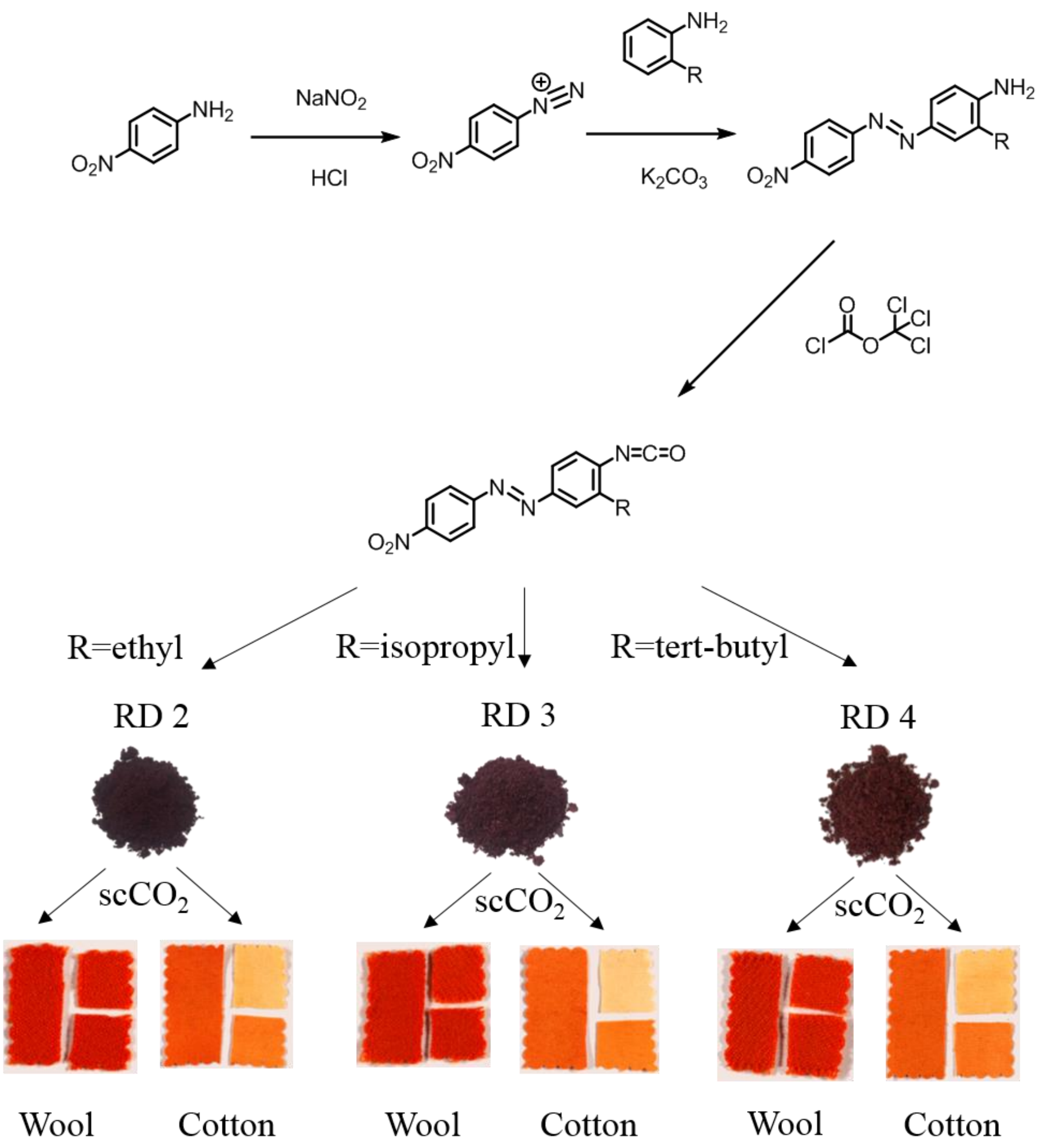


Figure 5.2 Graphical abstract of Chapter 5

5.2 Results and discussion

5.2.1 Dyeing wool fabric using RD 2, RD 3 and RD 4 in $scCO_2$

Synthesised CO_2 soluble RD 2, RD 3 and, RD 4 were used to dye natural fabrics in $scCO_2$. This section focused on the supercritical dyeing for wool using RD 2, RD 3 and RD 4. The colour depth, fixation and fastness properties were all evaluated and the results discussed. To assess how the temperature, pressure, dye loading (owf.), amount of water in the pre-treatment and the dyeing time affected the dyeing results, several different sets of experiments were undertaken. Investigations of these effects on the supercritical dyeing were carried out under the conditions outlined previously (Chapter 4). Increased pressures and dye loadings gave an increase in the dyeing quality. Thus, 140 bar and 5 % owf. of dye were used, as described below.

5.2.1.1 Investigation of the effect of water pre-treatment on the dyeing of wool using RD 2, RD 3 and RD 4

5 % owf. of RD 1, RD 2 and RD 3 respectively, with a pressure of 140 bar, and a temperature of 70 °C (60 minutes of dyeing time) were used in these series of supercritical dyeing experiments.

In Figure 5.3, the significant increase of colouration on the dyed wool fabrics is shown on the basis of the amount of water used in the pre-treatment process and dyeing process. After a 30 % owf. of water addition, the colour on the dyed wool fabrics plateaued. The fixation rate of the dyed wool fabrics followed this trend. The optimal results $[f_{k(dyed)} = 418.6, F = 93.6\ \%]$ were obtained at 30 % owf. of water addition. A positive influence of the water pre-treatment on the supercritical dyeing was observed, as in the previous studies (Chapter 4).

Similar situations are shown in Figure 5.4 and Figure 5.5. The optimal results $[f_{k(dyed)} = 458.1, F = 92.8\ \%]$ for RD 3 were obtained at 30 % owf. of water addition in the pre-treatment and dyeing process. With RD 4, the optimal results $[f_{k(dyed)} = 458.1, F = 92.8\ \%]$ were achieved at 40 % owf. of water addition. Some of the data were of slightly greater value than the stated maximal results, such as the fixation rate at 50 % (Figure 5.4) and the $f_{k(dyed)}$ value at 100 % (Figure 5.5). However, taking the factors of an ideal $f_{k(dyed)}$ value, great fixation and smallest possible amount of water being required in to account, the aforementioned optimal results were concluded.

The results of water additions in the pre-treatment process and its dyeing process show that water plays a very important role in the supercritical dyeing for wool. The introduction of alkyl groups can increase the solubility of the dyes in $scCO_2$. However, without water the dyeing qualities were still very poor, indicating that water was acting as a swelling reagent for wool rather than as a co-solvent increasing the polarity of $scCO_2$.

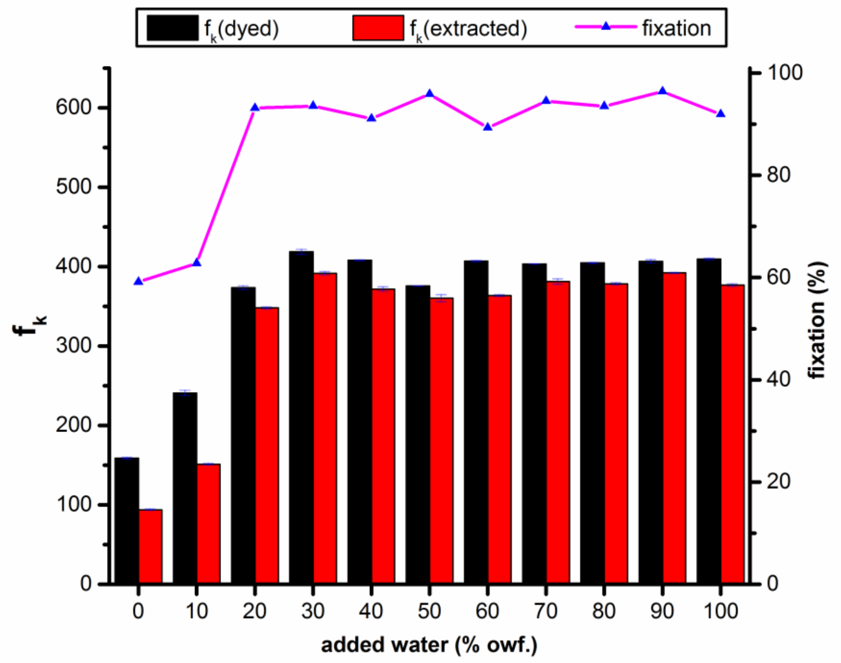


Figure 5.3 Effect of water addition in the pre-treatment process on the f_k value and the dye fixation of the wool dyed in scCO$_2$ with 5 % owf. of RD 2 at 70 °C, 140 bar for 60 minutes

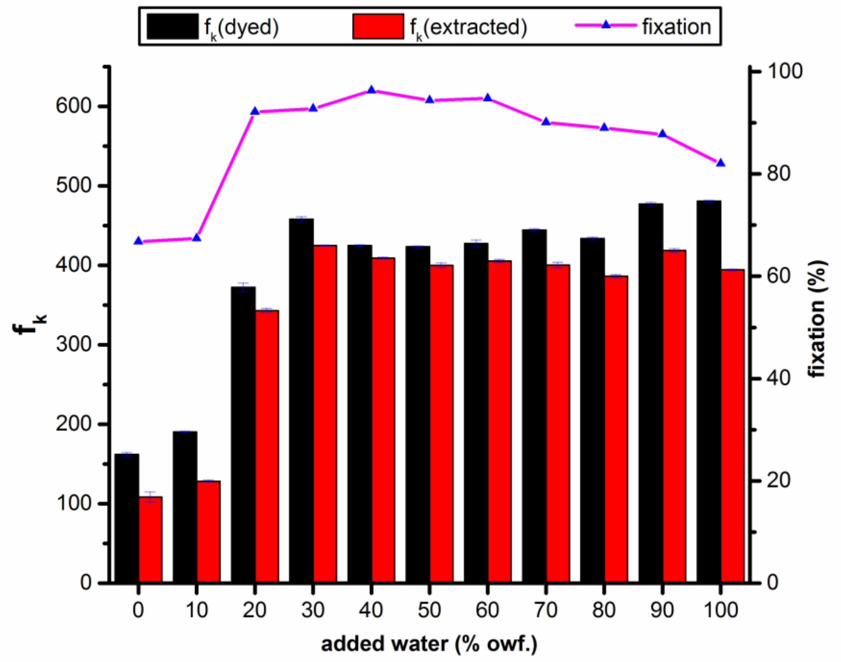


Figure 5.4 Effect of water addition in the pre-treatment process on the f_k value and the dye fixation of the wool dyed in scCO$_2$ with 5 % owf. of RD 3 at 70 °C, 140 bar for 60 minutes

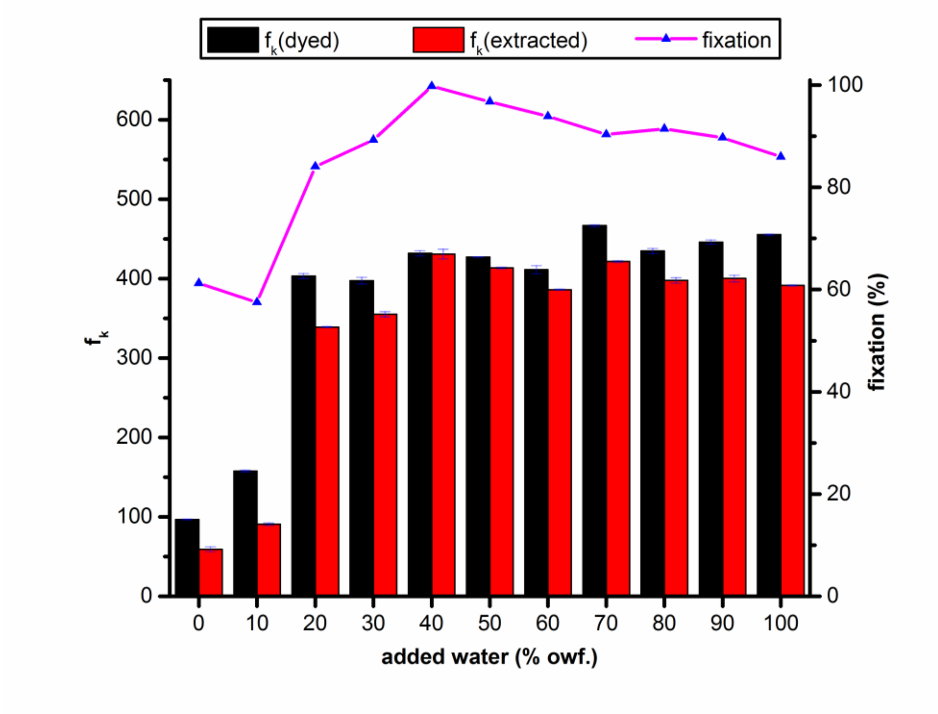


Figure 5.5 Effect of water addition in the pre-treatment process on the f_k value and the dye fixation of the wool dyed in $scCO_2$ with 5 % owf. of RD 4 at 70 °C, 140 bar for 60 minutes

5.2.1.2 Investigation of the effect of the temperature on the dyeing of wool using the RD 2, RD 3 and RD 4

Investigation of the effect of temperature on the supercritical dyeing of wool were undertaken using temperatures ranging from 40 °C to 100 °C at 10 °C intervals, 140 bar, with 5 % owf. of RD 2, RD 3 and RD 4 respectively, with 60 minutes of dyeing. These conditions were used for all of the three sets of experiments. In supercritical dyeing, using RD 2 and RD 3, 30 % owf. of water for the pre-treatment process was selected. In supercritical dyeing, using the RD 4, 40 % owf. of water was selected for the pre-treatment.

Figure 5.6 shows that temperature strongly influenced the colouration and the fixation of the dyed wool. The colouration and fixation increased with the increase in temperature up to 60 °C and then remained stable. Considering the issue of dyeing quality and the energy cost, the optimum colouration and fixation $[f_{k(dyed)} = 412.1, F = 94.1\ \%]$ were obtained at 60 °C.

Figure 5.7 illustrates that relatively good colouration and fixation results were achieved at lower temperatures (below 60 °C) when RD 3 was used in the supercritical dyeing. The colouration was increased from 163.7 at 40 °C to 458.1 at 70 °C rapidly. There was a minor decrease from 70°C, with a decrease in the fixation rate. The greatest colouration and greatest fixation ($f_{k(dyed)} = 458.1$, $F = 92.8$ %) on the dyed wool were obtained at 70 °C.

The colouration of wool dyed at 40 °C and at 50 °C were similar (Figure 5.8). Significant improvements were observed when the temperature was increased from 50 °C to 60 °C. After 60 °C, the $f_{k(dyed)}$ value was stable. In spite of variation in the fixation rate at 80 °C's, the trend was a rise with temperature which remained at this level after 70 °C. 70 °C gave the better results ($f_{k(dyed)} =$ 431.9, $F = 99.8$ %).

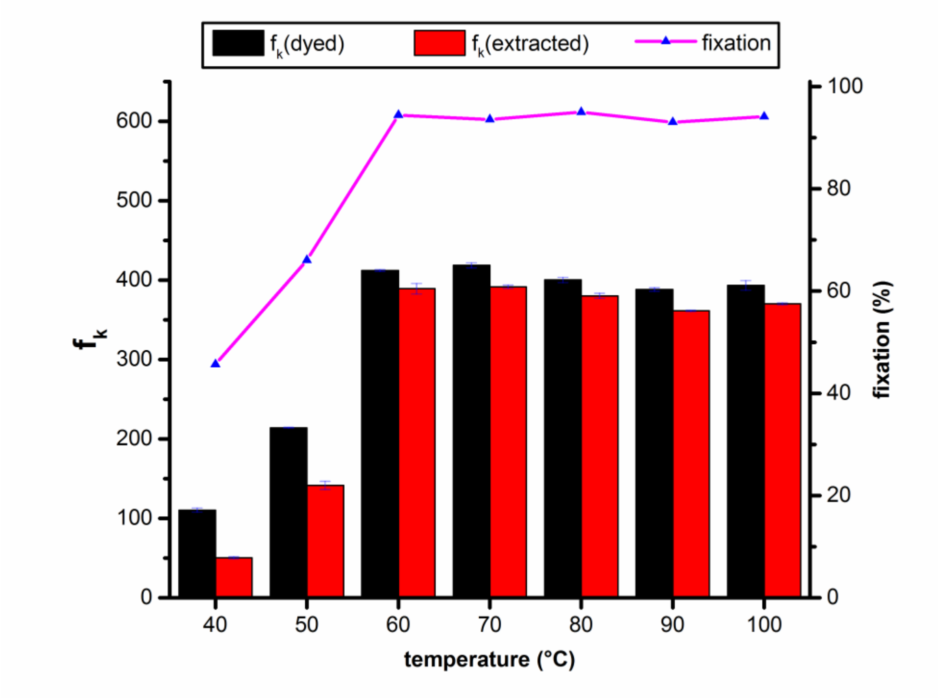


Figure 5.6 Effect of the temperature on the f_k value and on the fixation of dye of wool (30 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$ with 5 % owf. of RD 2 at 140 bar for 60 minutes

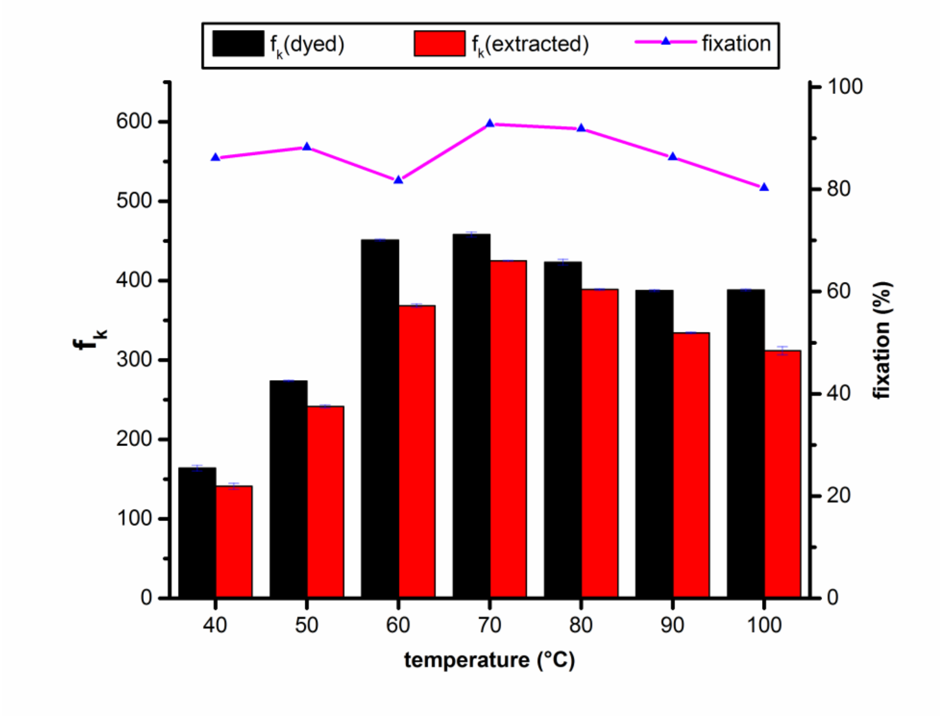


Figure 5.7 Effect of the temperature on the f_k value and on the fixation of dye of wool (30 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 3 at 140 bar for 60 minutes

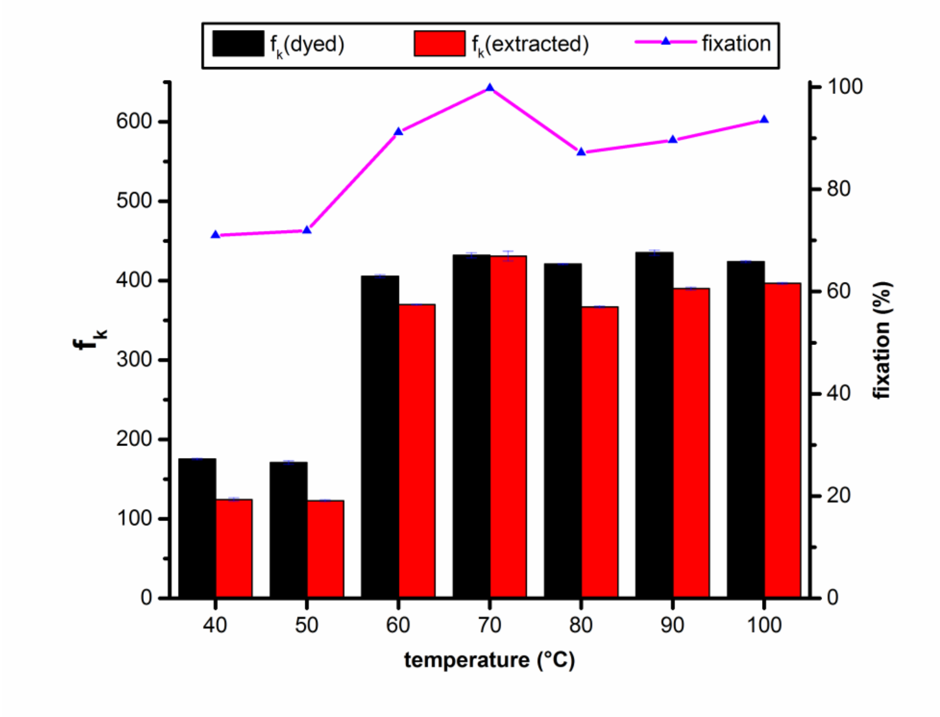


Figure 5.8 Effect of the temperature on the f_k value and on the fixation of dye of wool (40 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 4 at 140 bar for 60 minutes

With the addition of the ethyl group or the isopropyl group, to the chromophore, the optimal dyeing temperature was decreased by around 10 degrees compared to the results shown in Section 4.2.1.1. This may have been due to the increase of the solubility of the dye helping to create a more concentrated dye medium around the fabrics, in the supercritical fluid at low temperature.

5.2.1.3 Investigation of the effect of the dyeing time on the dyeing of wool using RD 2, RD 3 and RD 4

The optimal dyeing conditions for the supercritical dyeing of wool using three synthesised reactive disperse dyes, within 60 minutes were as follows: RD 2: 5 % owf. of dye, 30 % owf. of water in the pre-treatment process and dyeing process, 140 bar and 60 °C; RD 3: 5 % owf. of dye, 30 % owf. of water in the pre-treatment process and dyeing process, 140 bar and 60 °C; RD 4: 5 % owf. of dye, 40 % owf. of water in the pre-treatment process and in the dyeing process, 140 bar and 70 °C. In order to establish how the dyeing time impacted on the dyeing efficiencies, a series of experiments using one of the three dyes was carried out under the stated dyeing conditions for different known dyeing times.

Figure 5.9 shows that the longer dyeing times provided greater colouration. Excellent fixation on the dyed wool was achieved during this series of experiments. Good dyeing quality was obtained within 5 minutes. The fixation rate was around 90.0, Figure 5.9, even though the dyeing time was only 5 minutes. Improvements to the colouration of the dyed wool were observed between 5 to 40 minutes of dyeing. After around 40 minutes, the increase in colouration was slowed down, probably because the mobile phase of the wool fibre had been occupied by the dye. When the dyeing time was extended to 180 minutes, the colouration of the dyed wool tended to be stable. In this series of experiments the best dyeing results [$f_{k(dyed)} = 477.7$, $F = 92.0$ %] were achieved at 180 minutes.

As shown in Figure 5.10, the dyeing qualities of the wool dyed using RD 3 in $scCO_2$ improved considerably in the first 40 minutes. After 40 minutes, the fixation became steady at around 90.0 %. The $f_{k(dyed)}$ value increased smoothly up to 467.8 with the fixation rate of 90.6 %, at 180 minutes of dyeing time.

Figure 5.11 shows that both the $f_{k(dyed)}$ value and the fixation rate increased rapidly over the first 60 minutes of dyeing time. Under the stated dyeing conditions, the best results, using RD 4 in supercritical dyeing [$f_{k(dyed)} = 441.4$, $F = 94.1$ %], were obtained after 180 minutes.

The $f_{k(dyed)}$ values appeared to display a geometric logarithmic increase with the dyeing time. In order to compare the $f_{k(dyed)}$ value, $f_{k(dyed)} = 400$ showing a good colouration was termed as the “standard point”. With the help of the ethyl group, isopropyl group, or tert-butyl group, it took only around 30 minutes to reach the standard point. However, for dyeing with RD 1, the “standard point” was at 180 minutes. Potentially, the shorter dyeing time can save energy in industrial scale dyeing. The fixation rate was excellent after the “standard point” for all three of the dyes. For the dyeing with RD 2, 5 minutes dyeing time provided a good fixation rate (89.9 %).

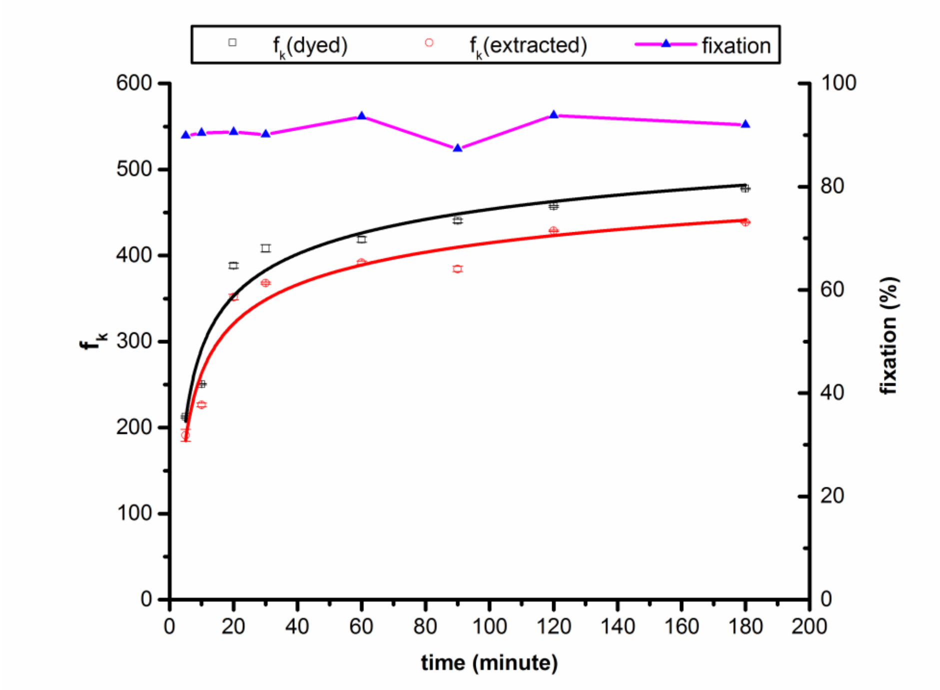


Figure 5.9 Effect of dyeing time on the f_k value and on the fixation of dye of wool (30 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$ with 5 % owf. of RD 2 at 60 °C, 140 bar

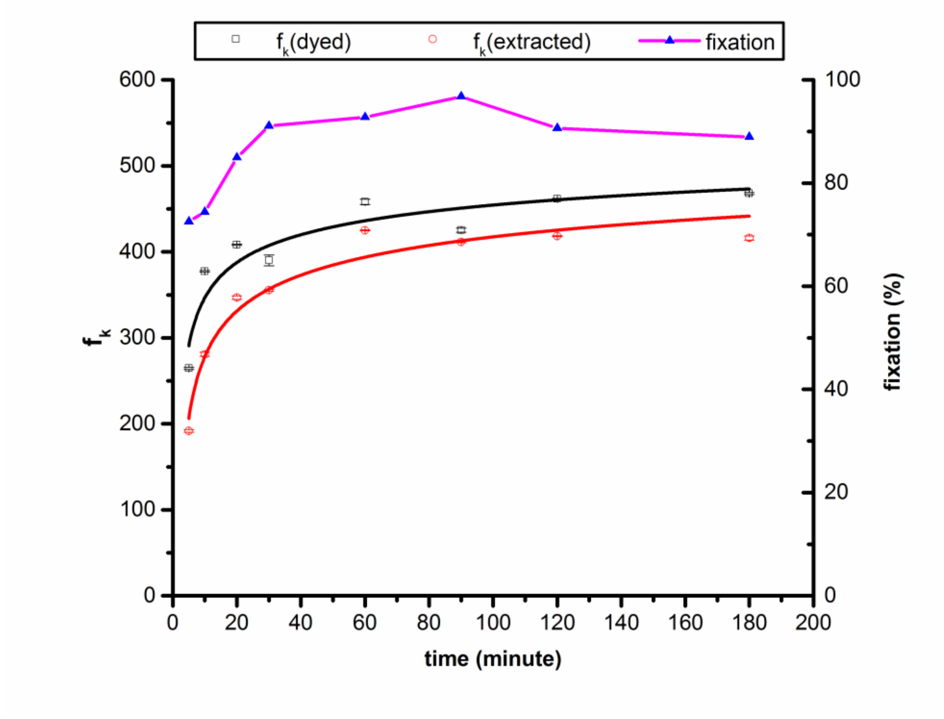


Figure 5.10 Effect of dyeing time on the f_k value and on the dye fixation of wool (30 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 3 at 70 °C, 140 bar

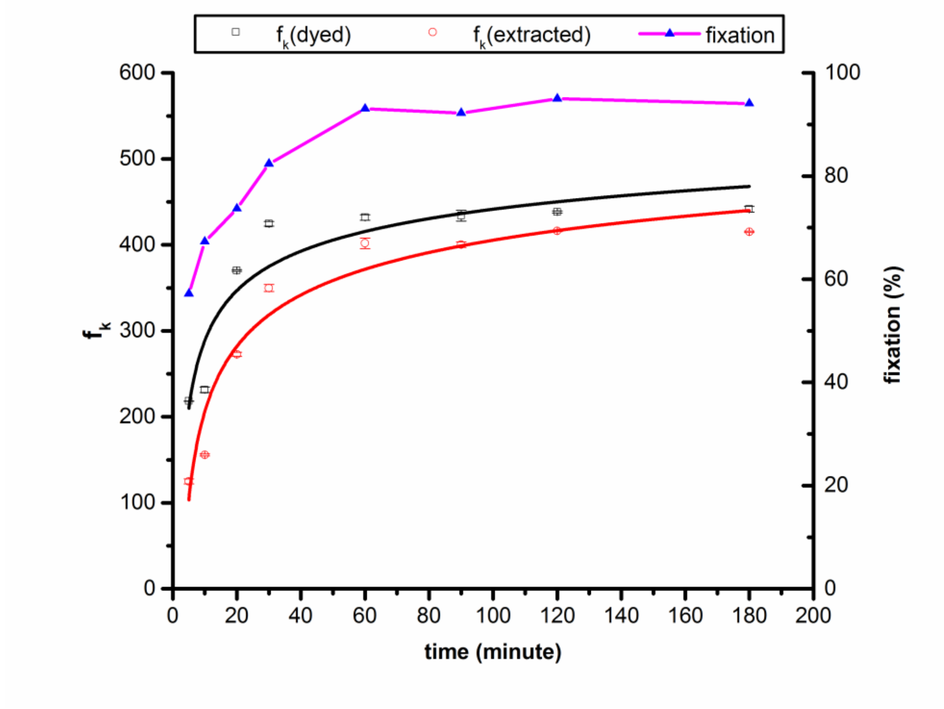


Figure 5.11 Effect of dyeing time on the f_k value and on the fixation of dye of wool (40 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 4 at 70 °C, 140 bar

5.2.1.4 Colour fastness testing

The wash fastness of wool fabrics dyed with RD 2, RD 3 and RD 4 under the dyeing conditions that showed the best results during varying dyeing times (Table 5.1, Table 5.2 and Table 5.3), were carried out according to the BS ISO 105-C06:2010 [10].

All three of the tables demonstrated similar wash fastness results. Superior staining fastness data were obtained. The covalent bonds between the dyes and the wool fabrics can provide a strong connection between each other. The fading fastness rate of the 10 minutes dyeing was 4 in all three tables, and might have been due to there being still some unreacted or hydrolysed dye on the surface of the fabrics in a short dyeing time. The little surface dye removed by washing was transferred onto the adjacent multifibres, mainly to acetate, nylon, acrylic and wool fabrics.

Table 5.1 The fastness of wool fabrics pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in scCO$_2$ at 60 °C, 140 bar at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	4	4	5	4-5	5	4-5	4-5
20	5	5	5	4-5	5	5	4-5
60	5	5	5	5	5	4-5	4-5
180	5	5	5	5	5	4-5	5

Table 5.2 The fastness of wool fabrics pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 3, in scCO$_2$ at 60 °C, 140 bar at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	4	4	5	4-5	5	4-5	4-5
20	5	5	5	4-5	5	5	4-5
60	5	5	5	5	5	4-5	4-5
180	5	5	5	5	5	4-5	5

Table 5.3 The fastness of wool fabrics pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 4, in $scCO_2$ at 70 °C, 140 bar at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	4	4	5	4-5	5	4-5	4-5
20	4	5	5	4-5	5	5	4-5
60	5	5	5	5	5	4-5	4-5
180	5	5	5	5	5	4-5	5

5.2.2 Dyeing cotton fabric using RD 2, RD 3 and RD 4 in $scCO_2$

Based on learning gain from previous results (Section 4.2.2.4), all of the dyeing experiments involved in investigating the optimum dyeing conditions of dyeing cotton in $scCO_2$, using RD 2, RD 3 and RD 4 respectively, were carried out with 5 % owf. of dye, at 140 bar.

5.2.2.1 Investigation of the effect of water pre-treatment on the dyeing of cotton using RD 2, RD 3 and RD 4

Within this study, the optimum temperature for cotton dyeing using RD 1 in $scCO_2$ was set to 60 °C. This temperature was selected on the basis of a series of experiments that were set up to study the effect of different quantities of water on the efficiency during the pre-treatment and dyeing processes. Figure **5.12**, Figure 5.13 and Figure 5.14 depict the colouration and fixation rate of dyed cotton fabrics using RD 2, RD 3 and RD 4 respectively, in supercritical dyeing system.

Similarly to previous results, (Section 4.2.2.4), water had an effect on both the colouration and the fixation during cotton dyeing in $scCO_2$. A slight increase in colour was observed and the fixation roughly increased by 3 % when water was used in the supercritical dyeing system (Figure **5.12**, Figure 5.13 and Figure 5.14). The optimal results were obtained at 30 % owf. of water addition (Figure **5.12**) [$f_{k(dyed)} = 188.3$, $F = 20.4$ %], 20 % owf. of water addition (Figure 5.13) [$f_{k(dyed)} = 176.2$, $F = 21.45$ %] and 40 % owf. of water addition (Figure 5.14) [$f_{k(dyed)} = 179.35$, $F = 21.9$ %]. Thus, the value of the optimal water addition in the pre-treatment and in the dyeing processes differed. However, the impact of using the different amounts of water was minor in supercritical cotton dyeing, using the three stated dyes.

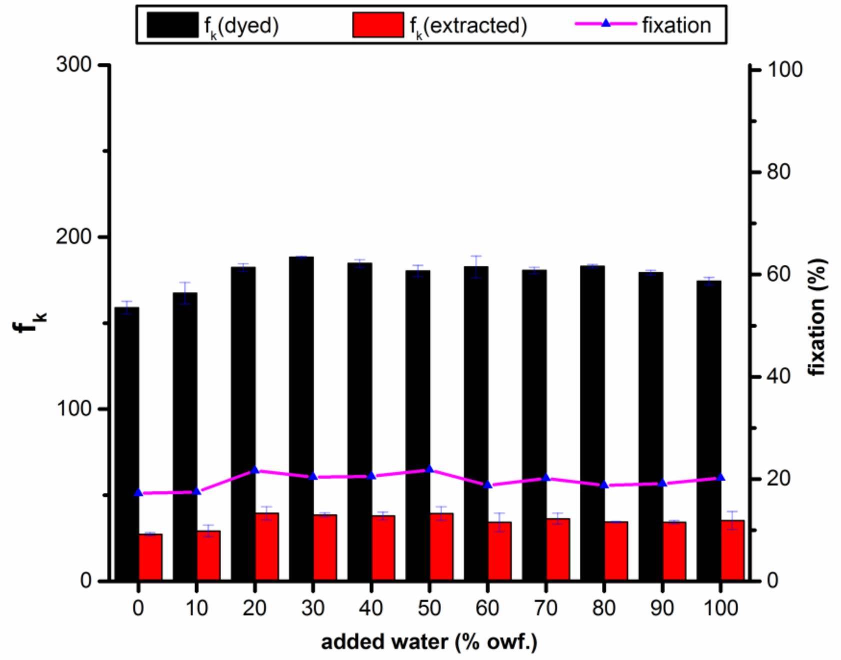


Figure 5.12 Effect of water addition on the pre-treatment process on the f_k value and on the dye fixation of the wool, dyed in $scCO_2$ with 5 % owf. of RD 2 at 60 °C, 140 bar, for 60 minutes

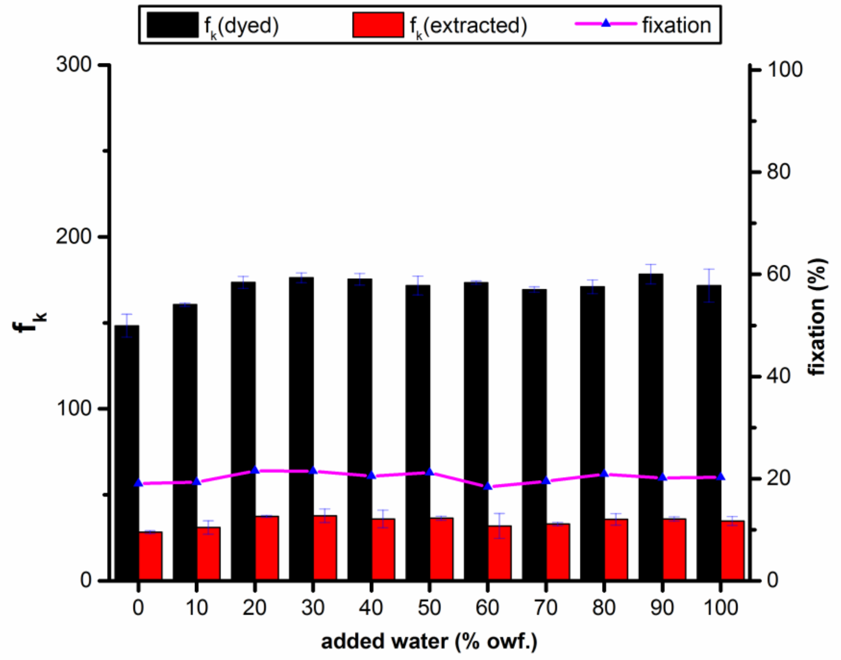


Figure 5.13 Effect of water addition on the pre-treatment process on the f_k value and on the dye fixation of the wool, dyed in $scCO_2$ with 5 % owf. of RD 3 at 60 °C, 140 bar, for 60 minutes

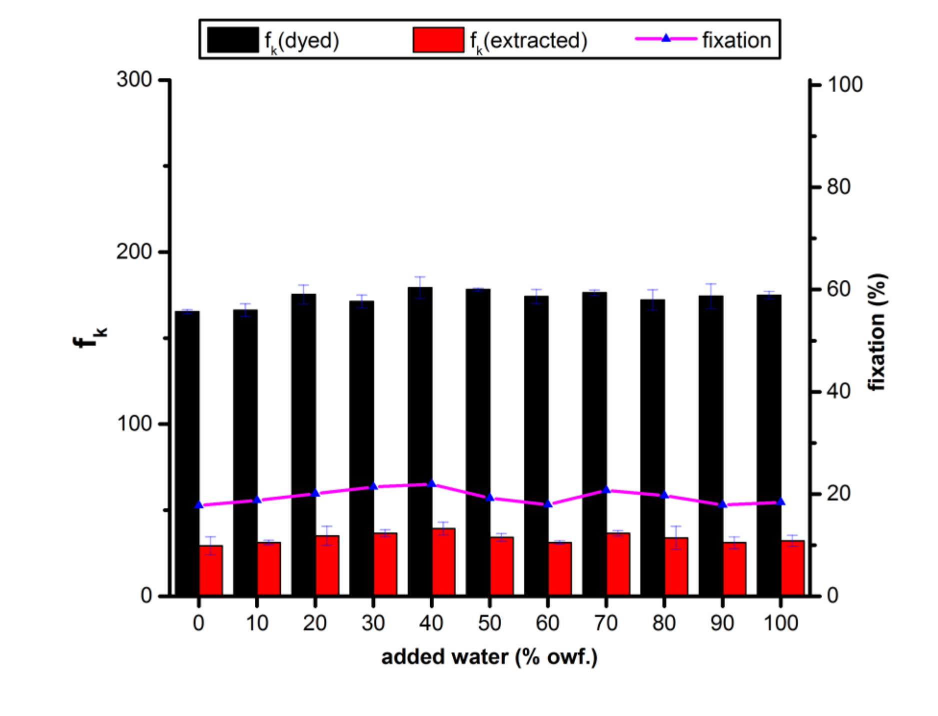


Figure 5.14 Effect of water addition on the pre-treatment process on the f_k value and on the dye fixation of the wool dyed, in scCO$_2$ with 5 % owf. of RD 4 at 60 °C, 140 bar, for 60 minutes

5.2.2.2 Investigation of the effect of the temperature on the dyeing of cotton using RD 2, RD 3 and RD 4

To evaluate the optimum dyeing temperature when using RD 2, RD 3 and RD 4 in the supercritical dyeing process, a series of experiments were undertaken at 140 bar with 5 % owf. of dye, the water amount being as discussed in Section 5.2.3.1, for 60 minutes of dyeing time.

Figure 5.15, Figure 5.16 and Figure 5.17 show the same trend in the colouration of the dyed cotton fabrics. The $f_{k(dyed)}$ value initially increased from a value of 100 at 40 °C to a value of 180 at 60 °C (Figure 5.15 and Figure 5.16) or at 70 °C (Figure 5.17). The $f_{k(dyed)}$ value then decreased. The fixation rate was approximately 20 % at all of the temperatures for all of the dyes.

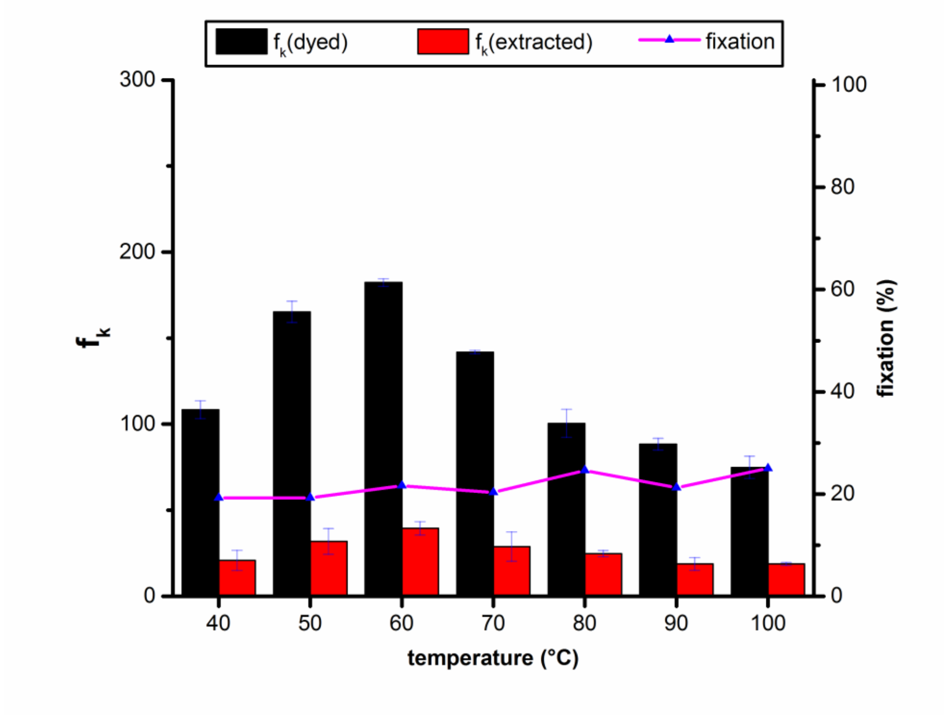


Figure 5.15 Effect of the operating temperature on the f_k value and on the dye fixation of cotton (30 % owf. of water, pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 2, at 140 bar, for 60 minutes

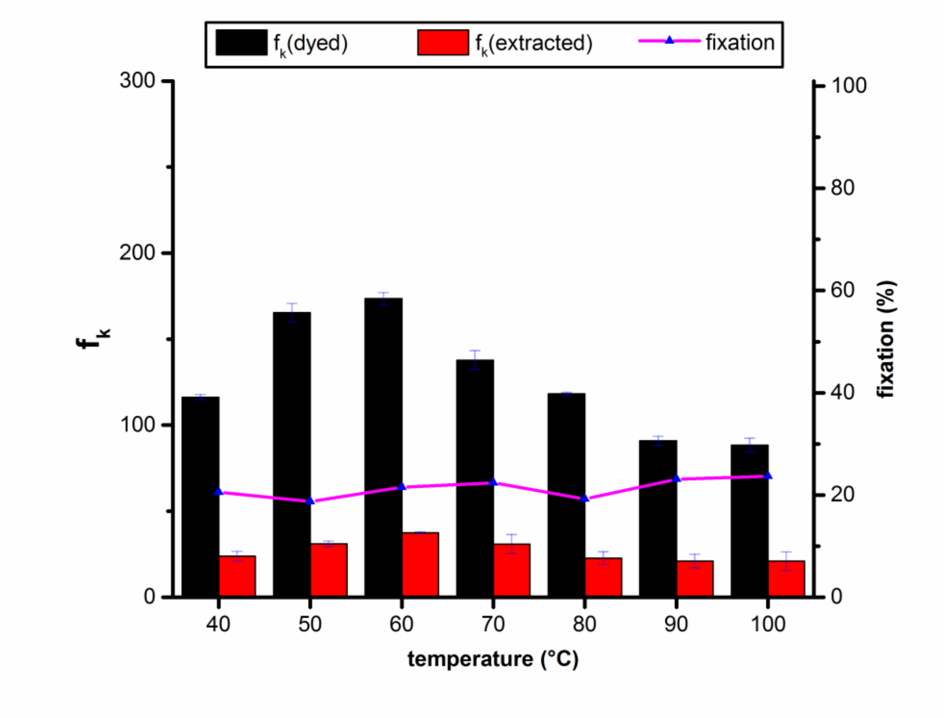


Figure 5.16 Effect of the operating temperature on the f_k value and on the dye fixation of cotton (20 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 3, at 140 bar, for 60 minutes

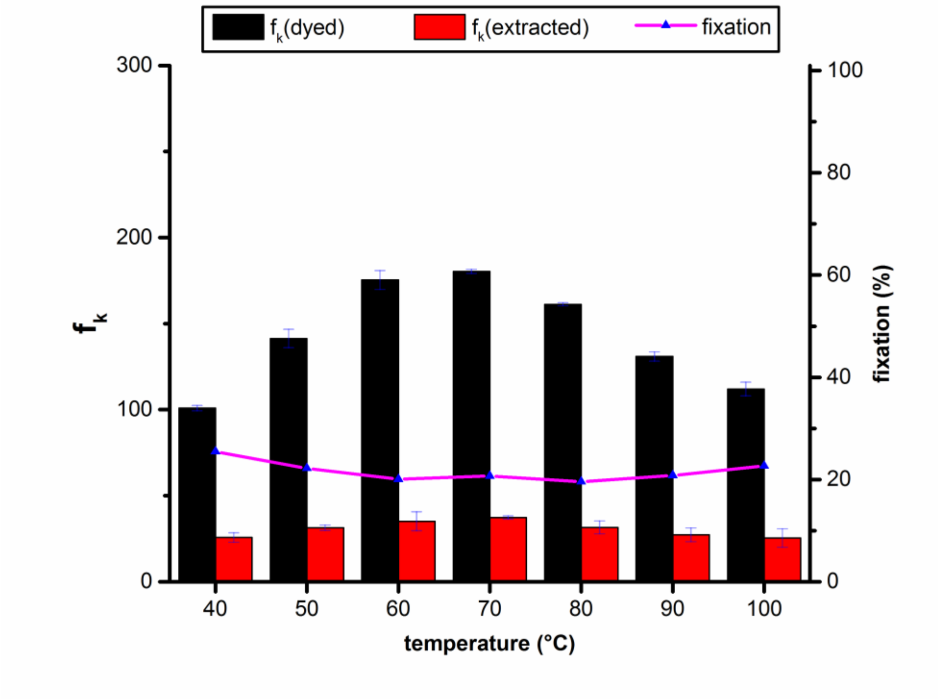


Figure 5.17 Effect of the operating temperature on the f_k value and on the dye fixation of cotton (40 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 4, at 140 bar, for 60 minutes

5.2.2.3 Investigation of the effect of dyeing time on cotton dyeing, using RD 2, RD 3 and RD 4

A time-based study of the cotton dyeing using RD 2, RD 3 and RD 4 in $scCO_2$ was carried out under the stated dyeing conditions for the three dyes (obtained from the Section 5.2.2.1 and Section 5.2.2.2).

The differences between in the results were very small for the cotton fabrics that were dyed using the three highly soluble dyes under the stated dyeing conditions. 5 minutes of dyeing gave results that showed a very poor colouration of the fabrics. The colour depth of the dyed cotton increased rapidly over the first 40 minutes, and then plateaued. The fixation stabilised at around 20 % after 40 minutes of dyeing indicating that after 40 minutes of dyeing, the dye might be almost hydrolysed. If any hydrolysed dye was attached to the cotton physically, increasing the colouration, it would be easily washed off by acetone:water (1:1) mixture. For the dyeing of cotton in $scCO_2$, the “standard point” was defined as the time that

$f_{k(dyed)}$ reached 180. In all of the three figures below, the "standard point" were at approximately 60 minutes. The best dyeing results, shown below, were obtained at 180 minutes, for all of the three dyes as expected. RD 2: $f_{k(dyed)} = 205.7$, $F = 20.2\ \%$, RD 3: $f_{k(dyed)} = 190.4$, $F = 21.5\ \%$, RD 4: $f_{k(dyed)} = 199.4$, $F = 20.2\ \%$.

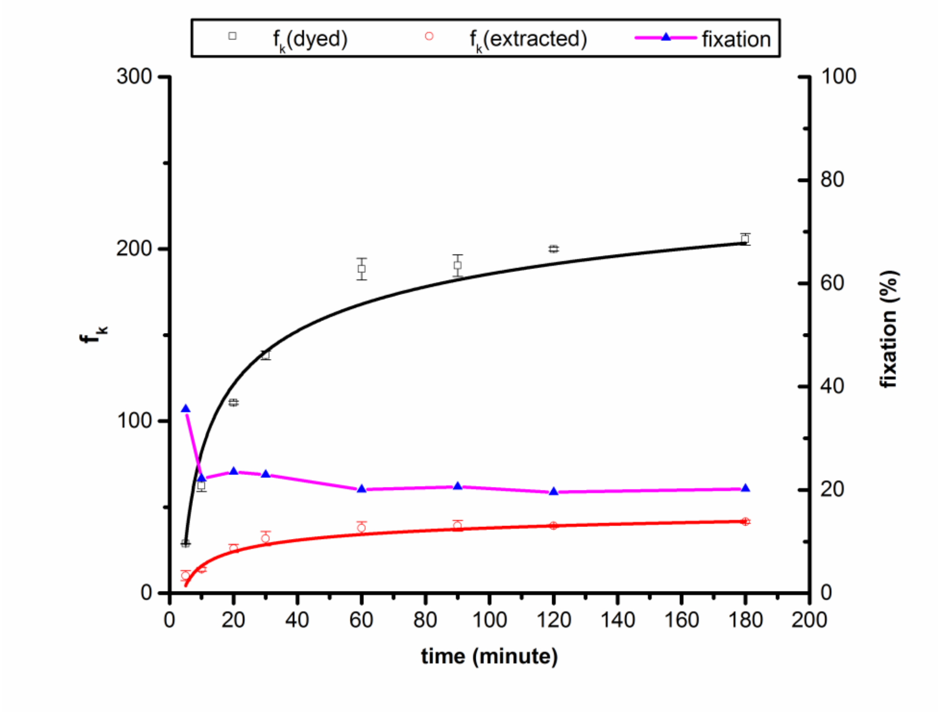


Figure 5.18 Effect of dyeing time on the f_k value and on the dye fixation on cotton (30 % owf. of water pre-treated for 30 minutes) dyed in scCO$_2$ with 5 % owf. of RD 2, at 60 °C, 140 bar

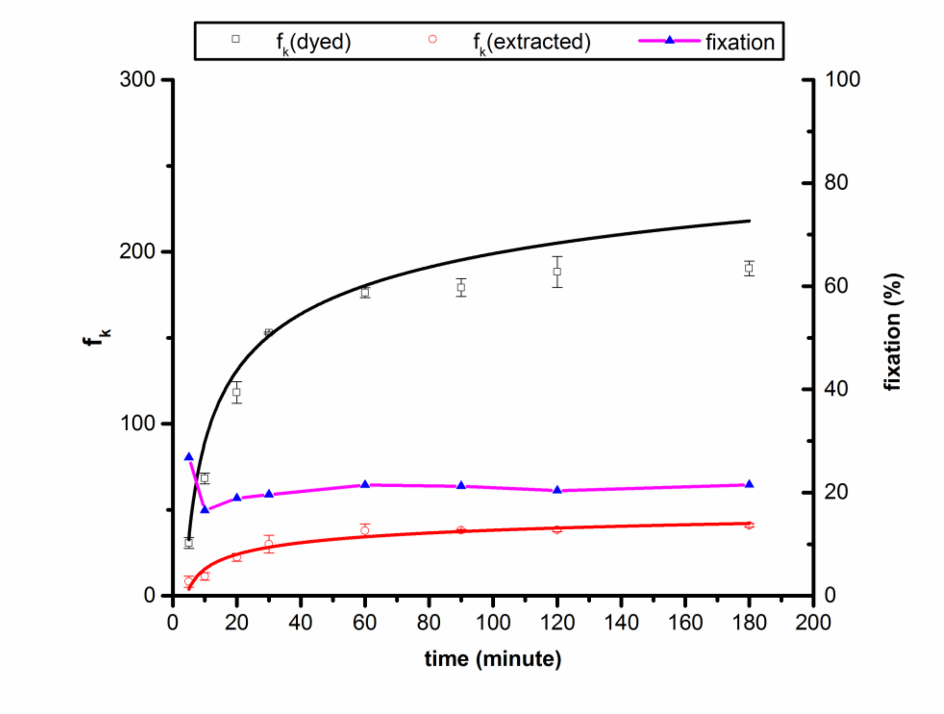


Figure 5.19 Effect of dyeing time on the f_k value and on the dye fixation on cotton (20 % owf. of water pre-treated for 30 minutes) dyed in $scCO_2$ with 5 % owf. of RD 3, at 60 °C, 140 bar

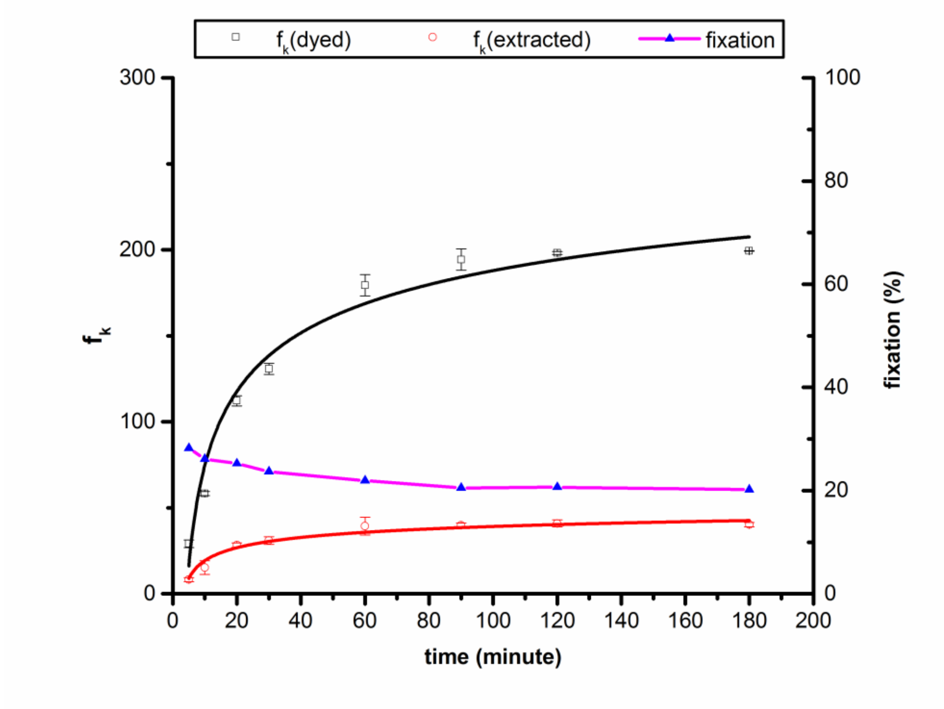


Figure 5.20 Effect of dyeing time on the f_k value and on the dye fixation on cotton, (40 % owf. of water pre-treated for 30 minutes), dyed in $scCO_2$ with 5 % owf. of RD 4, at 60 °C, 140 bar

5.2.2.4 Colour fastness testing

The colour fastness of cotton fabrics, dyed under the optimum conditions using RD 2, RD 3 and RD 4 (Table 5.4, Table 5.5 and Table 5.6) for various dyeing times was determined. The tests were carried out following the BS ISO 105-C06:2010 [10]. In the tables, the recorded results are shown to be very similar to the wash fastness shown in Section 4.2.2.6 when RD 1 was used for the supercritical dyeing for cotton fabrics. Good fading fastness was obtained after long dyeing times. However, the staining fastness on synthetic fabrics was not good. Any hydrolysed reactive disperse dye, being non-polar, would have good affinity to the synthetic fabrics.

Table 5.4 The fastness of cotton fabrics, pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in scCO$_2$ at 60 °C, 140 bar, at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	2	3-4	4	2	2	3	4
20	3-4	3-4	4	2	2	3	4
60	4	4	4	3	3	3	4
180	4	4	4	3	3	3	4

Table 5.5 The fastness of cotton fabrics, pre-treated with 20 % owf. of water, dyed with 5 % owf. of RD 2, in scCO$_2$ at 60 °C, 140 bar, at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	2	3-4	4	2	2	3	4
20	3-4	3-4	4	2	2	3	4
60	4	4	4	3	3	3	4
180	4	4	4	3	3	3-4	4

Table 5.6 The fastness of cotton fabrics, pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 2, in $scCO_2$ at 70 °C, 140 bar, at different dyeing times

Dyeing time (minutes)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	2	3-4	4	2	2	3	4
20	3-4	3-4	4	2	2	3	4
60	4	4	4	3	3	3	4
180	4	4	4	3	3	3	4

Noticeable differences in the depth of colouration between the extracted cotton fabrics and washed cotton fabrics were observed, Table 5.7, Table 5.8 and Table 5.9 displays $f_{k(\text{dyed})}$, $f_{k(\text{extracted})}$, $f_{k(\text{washed})}$, Fixation (extracted) and Fixation (washed). Though the overall fixation was unsatisfactory, a great improvement in the fixation was observed when the extraction process was replaced by a washing process. The three tables show very similar results, indicating that the introduction of ethyl, isopropyl and tert-butyl alkyl groups has a very similar effect on the supercritical dyeing of cotton fabric. Without organic solvent being present in the wash process, the relatively non-polar surface dye which had not reacted with fabrics would not be removed easily by the highly polar water. The maximum fixation rate increased to 81.5% (washed with water and detergent) from around 20 % [extracted with acetone:water (1:1)].

Table 5.7 f_k values of dyed cotton, of extracted cotton and of washed cotton fabrics, and fixation rate, using RD 2, at different dyeing times

Dyeing time (minute)	$f_{k(\text{dyed})}$	$f_{k(\text{extracted})}$	$f_{k(\text{washed})}$	Fixation (extracted)	Fixation (washed)
10	62.3	13.4	40.3	22.2 %	64.7 %
20	110.7	26.0	68.6	23.5 %	62.0 %
60	188.4	37.8	129.5	20.1 %	68.7 %
180	205.7	41.56	163.5	20.2 %	79.5 %

Table 5.8 f_k values of dyed cotton, of extracted cotton and of washed cotton fabrics, and fixation rate, using RD 2, at different dyeing times

Dyeing time (minute)	$f_{k(\text{dyed})}$	$f_{k(\text{extracted})}$	$f_{k(\text{washed})}$	Fixation (extracted)	Fixation (washed)
10	68.2	11.3	40.0	16.6 %	58.7 %
20	118.2	22.4	68.3	18.9 %	57.8 %
60	176.2	37.8	136.2	21.5 %	77.3 %
180	190.3	41.0	155.1	21.5 %	81.5 %

Table 5.9 f_k values of dyed cotton, of extracted cotton and of washed cotton fabrics, and fixation rate, using RD 2, at different dyeing times

Dyeing time (minute)	$f_{k(\text{dyed})}$	$f_{k(\text{extracted})}$	$f_{k(\text{washed})}$	Fixation (extracted)	Fixation (washed)
10	58.3	15.2	38.1	26.1 %	65.4 %
20	112.2	28.3	73.8	25.2 %	65.8 %
60	179.4	39.3	139.5	22.0 %	77.8 %
180	199.4	40.2	161.3	20.2 %	81.0 %

5.2.3 Microscopic study of wool and cotton dyed with RD 2, RD 3 and RD 4 in $scCO_2/H_2O$

5.2.3.1 SEM evaluation

Figure 5.21 presents SEM images of: (a) cotton fibres as supplied; (b) wool fibres as supplied; (c) cotton fibres pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (d) wool fibres pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (e) cotton fibres pre-treated with 20 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (f) wool fabric pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 70 °C, 140 bar for 180 minutes; (g) cotton fibres pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 70 °C, 140 bar for 180 minutes; (h) wool fabric pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 4, in $scCO_2$ at 70 °C, 140 bar for 180 minutes.

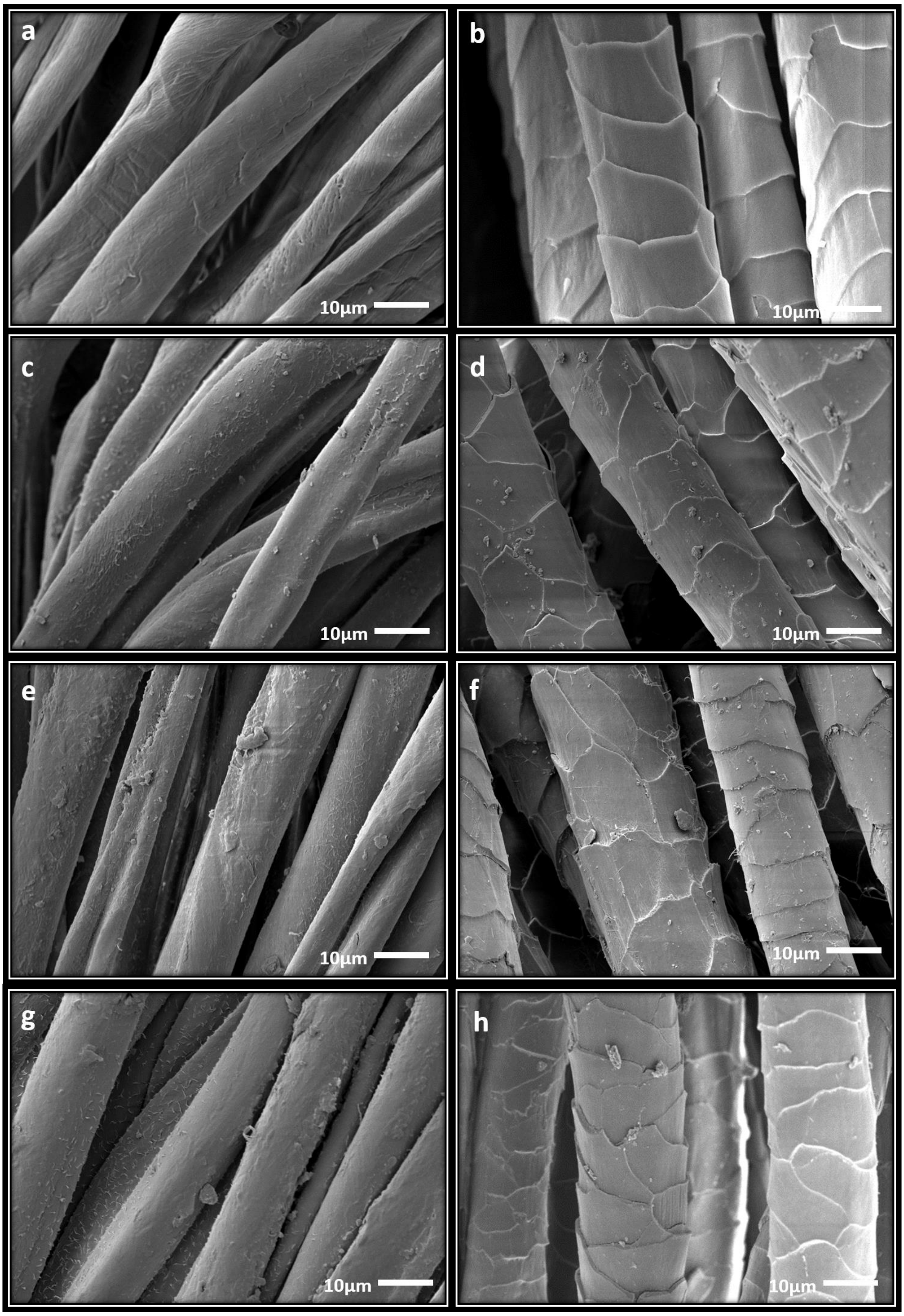


Figure 5.21 SEM images of the surface of cotton fibres, supplied wool fibres, and cotton fibres and wool fibres dyed under different conditions in scCO$_2$.

Figure 5.21c, Figure 5.21e, and Figure 5.21g demonstrate that some particles appeared on the surface of the dyed cotton fibres which were potentially the oligomeric dye precipitation. This phenomenon is very common for fibres dyed in $scCO_2$. Moreover, fibrillation and deep wrinkles can be clearly observed in the three images, indicating that the supercritical dyeing for cotton damaged the surface of the cotton fibres to varying degrees. In Figure 5.21g, the fibrillation is very obvious. The fibrillation of the fibre always appeared randomly in the supercritical dyeing for cotton using the isocyanate group containing reactive disperse dyes.

In Figure 5.21d, Figure 5.21f and Figure 5.21h, shows that the dyed wool fibres were relatively undamaged compared to the dyed cotton fibres. Some particles were scattered around on the wool scale. For the dyed wool fibres, the fragments and the scratches observed on the dyed wool fibres surface may have been caused by the physical contact between the magnetic stirrer and the fabrics in the supercritical dyeing machine for fluid circulation. No clear or serious damage was found on the dyed wool fibres.

5.2.3.2 Cross-section analysis

Figure 5.22 presents cross-section images of: (a) cotton fibres as supplied; (b) wool fibres as supplied; (c) cotton fibres pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (d) wool fibres pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 2, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (e) cotton fibres pre-treated with 20 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 60 °C, 140 bar for 180 minutes; (f) wool fabric pre-treated with 30 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 70 °C, 140 bar for 180 minutes; (g) cotton fibres pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 3, in $scCO_2$ at 70 °C, 140 bar for 180 minutes; (h) wool fabric pre-treated with 40 % owf. of water, dyed with 5 % owf. of RD 4, in $scCO_2$ at 70 °C, 140 bar for 180 minutes.

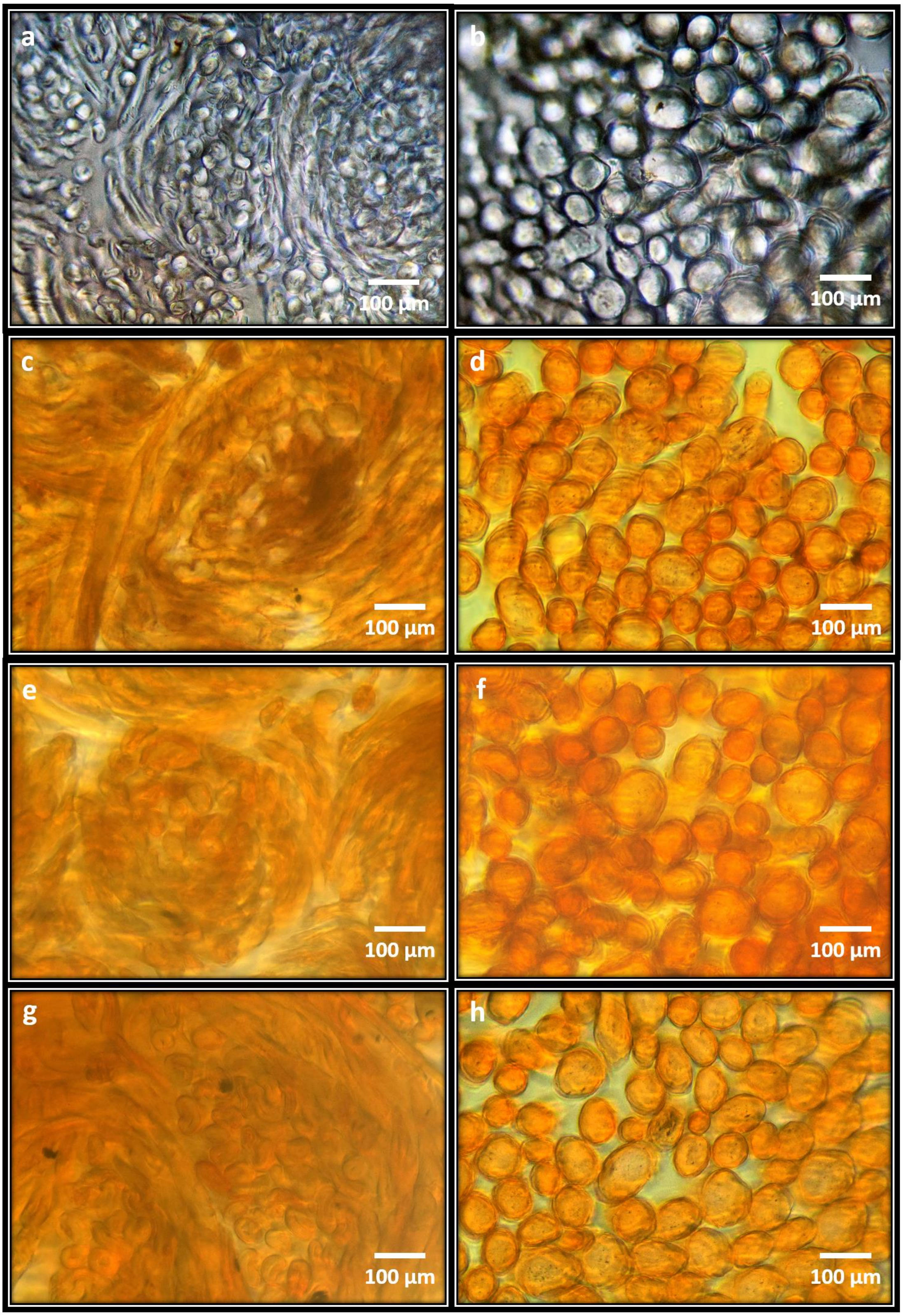


Figure 5.22 Cross-section images of the surface of cotton fibres, supplied wool fibres, and cotton fibres and wool fibres, and cotton fibres dyed under different conditions in scCO$_2$.

Generally, cotton has greater propensity to ring dyeing/unlevel dyeing than wool in supercritical dyeing under the stated conditions. Some blank spots were observed in the middle of fabrics shown in Figure 5.22b and Figure 5.22d indicating that ring dyeing occurred when RD 2 and RD 3 were used in the supercritical dyeing. Figure 5.22g dyeing levelness among the cotton dyeing. The cross-section images of wool have brighter colour and better levelness than those of cotton indicating that good penetration occurred in the dyeing of wool in $scCO_2$ under the stated conditions. Fibres in Figure 5.22f show a stronger orange than those shown in Figure 5.22d and Figure 5.22h corresponding to their f_k values.

5.2.4 Comparison of the best dyeing results of all these experimental conditions obtained when C.I. Disperse Orange 3, RD 1, RD 2, RD 3 and RD 4 were used in a supercritical dyeing study

5.2.4.1 Description of dyed samples and visual assessments

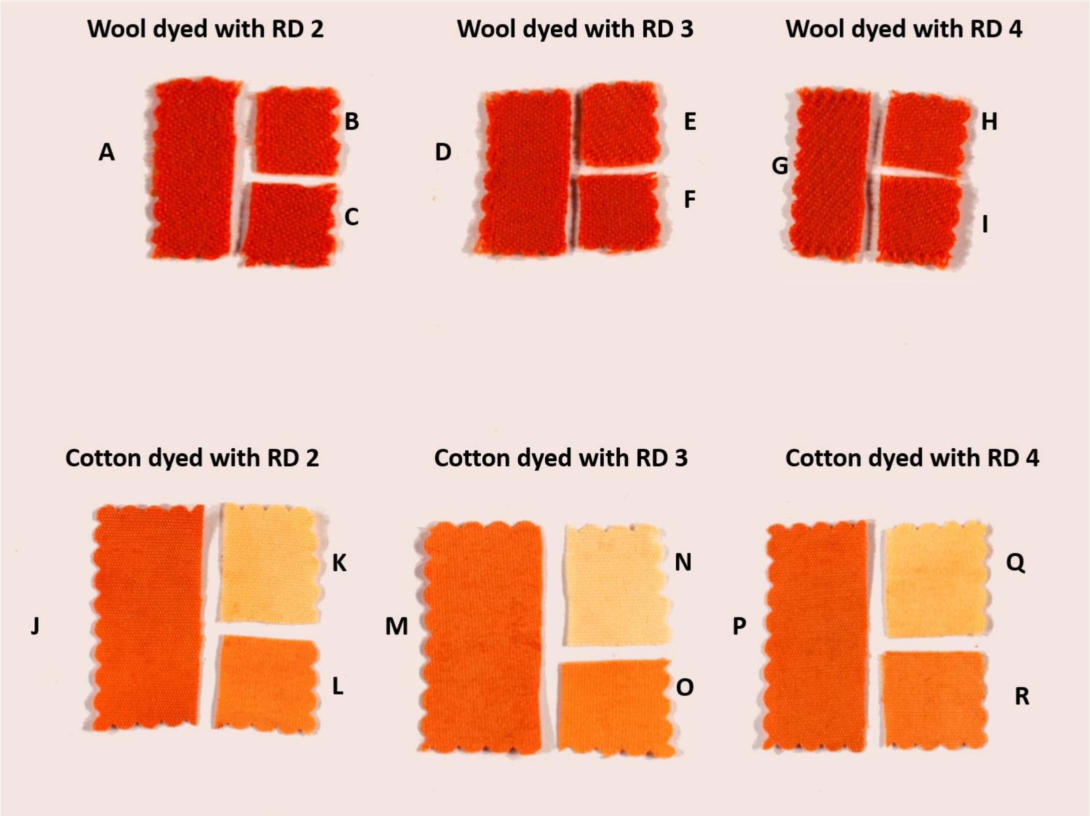


Figure 5.23 Dyed wool and cotton samples using RD 2, RD 3 and RD 4 in $scCO_2$

Figure 5.23 represented the dyed samples.

Fabric samples of A, B, C, J, K and L were dyed with RD 2. A: dyed wool sample; B: dyed wool sample extracted with acetone:water (1:1); C: dyed wool sample washed with water; J: dyed cotton sample; K: dyed cotton sample extracted with acetone:water (1:1); L: dyed cotton sample washed with water and detergent.

Fabric samples of D, E, F, M, N and O were dyed with RD 3. D: dyed wool sample; E: dyed wool sample extracted with acetone:water (1:1); F: dyed wool sample washed with water; M: dyed cotton sample; N: dyed cotton sample extracted with acetone:water (1:1); O: dyed cotton sample washed with water and detergent.

Fabric samples of G, H, I, P, Q and R were dyed with RD 3. G: dyed wool sample; H: dyed wool sample extracted with acetone:water (1:1); I: dyed wool sample washed with water; P: dyed cotton sample; Q: dyed cotton sample extracted with acetone:water (1:1); R: dyed cotton sample washed with water and detergent.

The dyeing conditions used were: Wool sample A - 60 °C, 140 bar, 5 % owf. of RD 2, 30 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time. Cotton sample J - 60 °C, 140 bar, 5 % owf. of RD 2, 30 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time. Wool sample D - 70 °C, 140 bar, 5 % owf. of RD 3, 30 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time. Cotton sample M - 60 °C, 140 bar, 5 % owf. of RD 3, 20 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time. Wool sample G - 70 °C, 140 bar, 5 % owf. of RD 4, 40 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time. Cotton sample P - 70 °C, 140 bar, 5 % owf. of RD 4, 40 % owf. of water pre-treatment for 30 minutes and 180 minutes dyeing time.

Strong colouration was observed for the dyed wool samples A, D and G (Figure 5.23). Most of the colour remained on the wool samples after the extraction and washing process. Dyed wool sample A whose dye that was modified with the ethyl group and isocyanate group had stronger colour than the dyed wool G containing the dyes having tert-butyl and isocyanate group. Moreover, the dyed wool fabrics based on dyes that were modified with the alkyl groups gave deeper colours than those sample dyed with RD 1, containing only the isocyanate reactive group.

Dyed cotton samples, Figure 5.23, had a very similar colour depth to those dyed with RD 1. A strong orange colour and level dyeing were obtained with the dyed cotton samples J, M and P. Samples L, O and R demonstrated that some of the colour had been washed off by the water and detergent in washing step. Also, when the dyed cotton was extracted with an organic solvent [acetone:water (1:1)], most of the orange colour was removed. The addition of the alkyl groups had little impact on the supercritical dyeing quality of cotton.

5.2.4.2 Colour [$f_{k(dyed)}$ value, fixation rate and CIE L*a*b* value] of RD 2, RD 3 and RD 4 on wool fabrics and on cotton fabrics

Table 5.10 CIE L*a*b* values of dyed wool fabrics and of dyed cotton fabrics, dyed using the stated dyeing conditions, for 180 minutes

Sample	L^*	a^*	b^*
Wool (Figure 5.23A)	39.17	49.52	51.55
Cotton (Figure 5.23J)	49.81	40.10	45.31
Wool (Figure 5.23D)	40.39	50.13	52.62
Cotton (Figure 5.23M)	50.21	40.18	44.96
Wool (Figure 5.23G)	41.01	50.42	53.17
Cotton (Figure 5.23P)	50.28	40.23	45.10

The CIE L*a*b* colour space value are summarised in Table 5.10. The table indicates similar colour characteristics in the orange hue of all the dyed cotton and dyed wool samples, respectively.

5.2.4.3 Comparison of the best results when C.I. Disperse Orange 3, RD 1, RD 2, RD 3 and RD 4 were used in the supercritical dyeing processes, respectively

Table 5.11 presents results obtained through dyeing using different dyes in supercritical dyeing processes after 180 minutes of dyeing time.

For the dyeing of wool in $scCO_2/H_2O$, it is clear that with the introduction of the isocyanate group into the dye molecule, the colour and fixation rate of the dyed wool improved. The $f_{k(\mathrm{dyed})}$ value was doubled when RD 1 was used instead of C.I. Disperse Orange 3. This indicates that the addition of the alkyl groups onto the chromophore molecule helped to enhance the dyeing ability of the reactive disperse dyes. The $f_{k(\mathrm{dyed})}$ value of the dyed wool fabrics was increased to 477.7, 467.8 and 441.4 from 400.9, when one of the ethyl, isopropyl, and tert-butyl groups was introduced to the dye molecule respectively. This may have been caused by the increase of the solubility of the dye in $scCO_2$ and hence the increase in the dye uptake. The fixation rate remained at around 90 %, changing slightly on introducing the alkyl groups to the reactive disperse dye.

For the cotton dyeing in $scCO_2/H_2O$, the fixation was increased from 13.8 % to 17.7 % when the dye containing the isocyanate group was used in the dyeing. A slight improvement was observed by inclusion of the alkyl groups. However, the alkyl groups had little impact on the colour of the dyed cotton.

Table 5.11 $f_{k(dyed)}$ value and the fixation rates of the wool fabrics and of the cotton fabrics dyed using C.I. Disperse Orange 3, RD 1, RD 2, RD 3 and RD 4 respectively, under their stated dyeing conditions in $scCO_2$ for 180 minutes of dyeing time

	Wool		**Cotton**	
	$f_{k(dyed)}$	**Fixation (extracted)**	$f_{k(dyed)}$	**Fixation (extracted)**
C.I Disperse Orange 3	201.4	60.1 %	91.4	13.8 %
RD 1	400.9	92.7 %	199.2	17.7 %
RD 2	477.7	92.0 %	205.7	20.2 %
RD 3	467.8	90.6 %	190.3	21.5 %
RD 4	441.4	94.1 %	199.4	20.2 %

The stated dyeing conditions are presented in Table 5.12 and in Table 5.13. The chosen dye loading in $scCO_2$ (5 % owf.) and the optimum pressure (140 bar) were the same in this study. The tables listed below only provide the value of the chosen temperature, standard point of time and the optimum water addition in the pre-treatment and dyeing processes.

With the introduction of the ethyl group and tert-butyl groups into the dye, less water was needed to achieve the best results of all these experimental conditions, in supercritical dyeing for wool. Even though the water addition was 10 % more than with the unmodified C.I. Disperse Orange 3, RD 1 gave a stronger colour to the dyed wool fabric. Moreover, with the help of the alkyl groups, the dyeing time needed for the wool to reach the “standard point” was reduced significantly from 180 minutes to 30 minutes. This indicated that the increase in the solubility could possibly accelerate the dyeing process.

Generally, Table 5.13, the dyeing temperature to obtain the best results was decreased by 10 °C through the introduction of the isocyanate reactive group and the alkyl groups to the C.I. Disperse Orange 3. The chosen dyeing temperature for wool using RD 4 did not change. However, RD 4 provided a stronger colour and a greater fixation rate. The times required to reach the “standard point” were all the same for all of the synthesised dyes. The water consumption was increased when the C.I. Disperse Orange 3 was modified by the isocyanate and alkyl groups. However, the colouration and the fixation rates were improved. The results indicated that the isocyanate group on the dye molecule helped improve the dyeing quality for cotton in $scCO_2$. However, for the reactive disperse dye containing the isocyanate group, increasing the solubility of the dye was not shown to affect the dyeing quality for cotton dyeing in $scCO_2$.

Table 5.12 The chosen dyeing temperature and the amount of water addition in the pre-treatment and dyeing process, when the best results were obtained, and the time to reach the "standard point" for wool dyeing using different dyes in $scCO_2$

	Temperature	**Time (standard point)**	**Water addition**
C.I. Disperse Orange 3	70 °C	n/a	40 % owf.
RD 1	70 °C	180 minutes	50 % owf.
RD 2	60 °C	30 minutes	30 % owf.
RD 3	70 °C	30 minutes	30 % owf.
RD 4	70 °C	30 minutes	40 % owf.

Table 5.13 The chosen dyeing temperature and the amount of water addition in the pre-treatment and dyeing process, when the best results were obtained, and the time to reach the "standard point" for cotton dyeing using different dyes in $scCO_2$

	Temperature	**Time (standard point)**	**Water addition**
C.I. Disperse Orange 3	70 °C	n/a	10 % owf.
RD 1	60 °C	60 minutes	20 % owf.
RD 2	60 °C	60 minutes	30 % owf.
RD 3	60 °C	60 minutes	20 % owf.
RD 4	70 °C	60 minutes	40 % owf.

5.3 Conclusions

Three novel modified disperse dyes used to form reactive disperse dyes were synthesised successfully. These were modified successfully to give three novel reactive disperse dyes. This was the first time that such dyes had been introduced for supercritical dyeing to increase the solubility of the dye molecules in $scCO_2$.

Each of the reactive disperse dyes was used to dye wool fabrics and cotton fabrics in $scCO_2$. The addition of solubilising groups to the dye molecules increased the access of the dyes in $scCO_2$ for wool fabrics.

The dyed wool fabrics using these dyes gave excellent results in colour strength, fixation and wash fastness (fading and staining). For the isocyanate group modified RD 1, the colour of the dyed wool fabrics was improved by introducing the alkyl groups to various extents. The best results including colouration $[f_{k(dyed)} = 477.7]$ were obtained when RD 2 was used in the supercritical dyeing of wool fabrics. The fixation rate remained at a high level (around 90 %) and was not affected by the additional alkyl groups.

Dyeing experiments were also carried out under different dyeing conditions to establish the appropriate dyeing conditions for cotton dyeing in $scCO_2$. The cotton dyeing results were not improved by the introduction of the alkyl groups on the dye molecule, indicating that in this study, the solubility of the dyes in $scCO_2$ did not enhance the dyeing of cotton when the reactive group of the dye was not suitable in supercritical dyeing conditions. Moreover, the inability to swell the cotton is still a big obstacle for the supercritical dyeing of cotton.

The SEM images show that the supercritical dyeing process using dyes containing the isocyanate group damaged the cotton fabrics surfaces giving fibrillation. The SEM images of the dyed wool fabrics demonstrated slight damage to the wool. Particles of the dye oligomer could also be found on the surface of the dyed cotton fibres and wool fibres.

Finally, the supercritical dyeing for wool fabrics was achieved successfully by introducing the isocyanate group and the alkyl groups to the traditional disperse dye.

5.4 References

1. Long, J.-J., Y.-Q. Ma, and J.-P. Zhao, *Investigations on the level dyeing of fabrics in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2011. **57**(1): p. 80-86.
2. Fernandez Cid, M.V., J. van Spronsen, M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *A significant approach to dye cotton in*

supercritical carbon dioxide with fluorotriazine reactive dyes. The Journal of supercritical fluids, 2007. **40**(3): p. 477-484.

3. Khatri, A., M.H. Peerzada, M. Mohsin, and M. White, *A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution.* Journal of Cleaner Production, 2015. **87**: p. 50-57.
4. Funazukuri, T., S. Hachisu, and N. Wakao, *Measurements of binary diffusion coefficients of C16-C24 unsaturated fatty acid methyl esters in supercritical carbon dioxide.* Industrial & engineering chemistry research, 1991. **30**(6): p. 1323-1329.
5. Bach, E., E. Cleve, and E. Schollmeyer, *Past, present and future of supercritical fluid dyeing technology–an overview.* Review of Progress in Coloration and Related Topics, 2002. **32**(1): p. 88-102.
6. Draper, S.L., G.A. Montero, B. Smith, and K. Beck, *Solubility relationships for disperse dyes in supercritical carbon dioxide.* Dyes and Pigments, 2000. **45**(3): p. 177-183.
7. McHugh, M.A., A. Garach-Domech, I.-H. Park, D. Li, E. Barbu, P. Graham, and J. Tsibouklis, *Impact of fluorination and side-chain length on poly (methylpropenoxyalkylsiloxane) and poly (alkyl methacrylate) solubility in supercritical carbon dioxide.* Macromolecules, 2002. **35**(17): p. 6479-6482.
8. Rindfleisch, F., T.P. DiNoia, and M.A. McHugh, *Solubility of polymers and copolymers in supercritical* CO_2*.* The Journal of Physical Chemistry, 1996. **100**(38): p. 15581-15587.
9. Sarbu, T., T. Styranec, and E.J. Beckman, *Non-fluorous polymers with very high solubility in supercritical* CO_2 *down to low pressures.* Nature, 2000. **405**(6783): p. 165-168.
10. ISO, Textiles-Tests for colour fastness-Colour fastness to domestic and commercial laundering, British Standards Institution(BSI Group), London, UK, 2010.

Chapter 6 Dyeing natural fabrics with the reactive disperse dye containing vinyl sulphonyl group

6.1 Introduction

6.1.1 Background

One of the more promising concepts that could overcome the limitation of the already highlighted techniques mentioned is the use of $scCO_2$ soluble disperse dyes that have been modified with a highly reactive functional group [1]. 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. Another advantage of using such dyes is that they are non-polar, allowing direct solubilisation in $scCO_2$. Many different reactive groups have been reported for dyeing of natural fibres. Reactive dyes containing vinyl sulphonyl group that can be used in conventional without alkali has a great potential to be applied in the supercritical dyeing.

The objective of this study was to synthesise an azo based disperse dye containing vinyl sulphonyl reactive group, and apply the synthesised dye in a natural fabric dyeing process using an eco-friendly supercritical dyeing technology. Amine groups on the side chains of the amino acids in wool fabric and hydroxyl groups in the cotton cellulose fabrics are reactive to the vinyl sulphonyl reactive dyes under a wide range of conditions [2]. Vinyl sulphone modified disperse dyes have been synthesised to dye natural fabrics and nylon as indicated in the literature [3-5]. Good dyeing results were obtained for wool and nylon in presence of some water. Long *et al*. claimed that cotton cannot be dyed properly without a catalyst because the reactivity of amine groups being greater than hydroxyl groups and the inability of the swelling of cotton in $scCO_2$.

6.1.2 Rationale

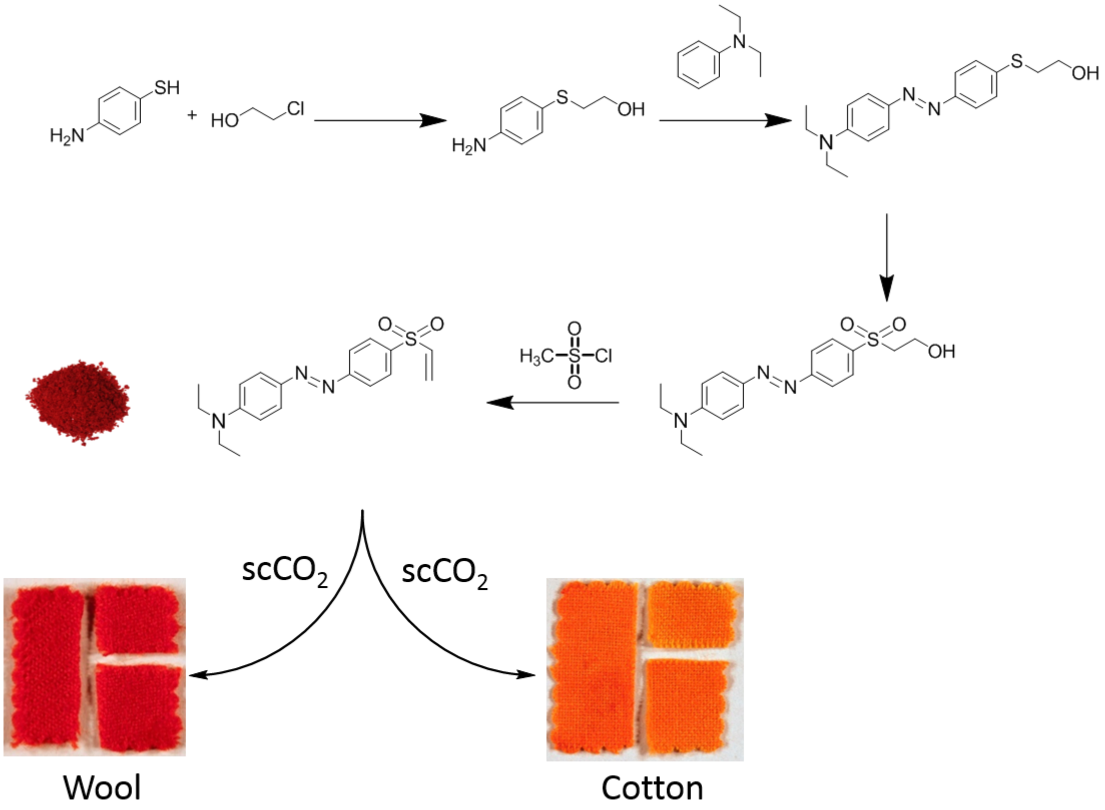


Figure 6.1 Graphical abstract of Chapter 6

This study provided a simple route to the synthesis of a vinyl sulphonyl 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 could save around half of the energy according to industrial expert [6].

This study provides a new synthesis route presented in Figure **6.1**, for an azo-based disperse reactive dye containing vinyl sulphonyl reactive group. The vinyl sulphonyl contained RD 5 is able to dye natural fibres using supercritical carbon dioxide as the dyeing medium. The optimum dyeing process was carried out with 30 minutes water pre-treatment and dyeing at 90 °C and 140 bar during a 60 minutes dyeing time. Under optimal conditions, which are relatively moderate in general supercritical dyeing processes, the dyed natural fabrics produced uniform dyeings with high colour strength and good fastness properties that were comparable to those from conventional aqueous dyeing. Furthermore, there was the potential to modify a wide scope of disperse dyes using the thiol group via this synthetic method.

6.2 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 the results shown in Chapters 4 and 5, and the previous studies [7, 8], a greater pressure lead 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 more dye was dissolved as the pressure was increased [7, 9, 10]. Dyes absorbed by the fibres would not migrate back to the carbon dioxide phase easily due to the formation of the covalent bonds between dyes and fibres. As the previous researches were carried out under high pressure systems (>200 bar), all experiments in this study were conducted under lower pressure (140 bar) to balance the dyeing qualities and the cost of operation.

In the previous work (Chapter 4 and 5) [3, 4, 11], water pre-treatment and water addition were shown to improve the dyeing results dramatically. The dyeing time and temperature had a great impacts on the dyeing qualities [1]. 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 5.

6.2.1 Dyeing wool fabric using RD 5 containing vinyl sulphonyl group

6.2.1.1 Investigation of the effect of water pre-treatment on dyeing of wool, using the RD 5 containing vinyl sulphone

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 a 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 % owf. of RD 5 and different amount of water, during a 60 minute period.

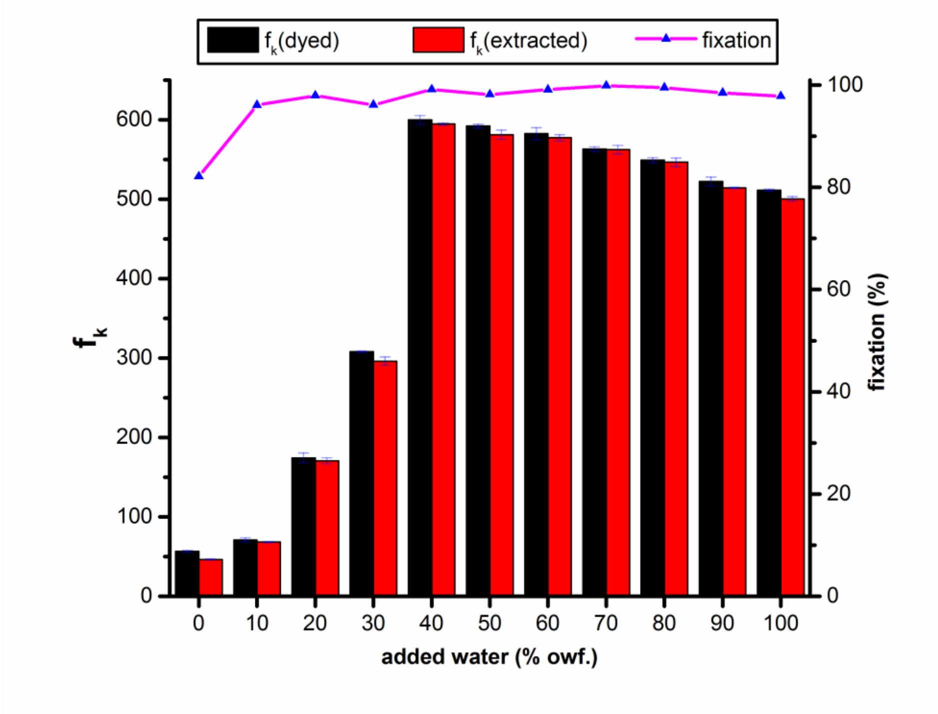


Figure 6.2 Effect of water pre-treatment on wool fabric on the f_k value and the dye fixation dyed in scCO$_2$ with 5 % owf. of RD 5 at 90 °C, 140 bar for 60 minutes

As seen in Figure 6.2, 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 % owf. 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% owf. can be attributed to either the competitive reaction between wool fibre and water, or the over density of the supercritical fluid which would leads to a lower solubility of the synthesised reactive disperse dye. Excellent fixation rates ($F > 96\%$) were obtained after adding only 10 % owf. of water. The greatest fixation rate of 99.9 was obtained when wool was dyed with 70 % owf. 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 $scCO_2$ due to the water pre-treatment. The density of the $scCO_2$ increases with the increase of water amount in this $scCO_2$-rich phase [12]. As the synthesised dye in $scCO_2$ can be easily dissolved in acetone that has the density between water and CO_2, the synthesised dye potentially can be dissolved in water and CO_2 mixture. Thus, the solubility of the dye was increased initially with a small amount of water in the supercritical vessel then decreased. The little water addition 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 [3].

6.2.1.2 Investigation of the effect of the temperature on the dyeing of wool, using the RD 5 containing vinyl sulphone

In the previous study of the effect of water pre-treatment, the best dyeing quality was obtained with fabrics containing 40 % owf. 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 % owf. of synthesised RD 5, the fabric containing 40 % owf. of water, during a 60 minute dyeing period.

A significant improvement in the extent of fixation was observed, as seen in Figure 6.3, 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.

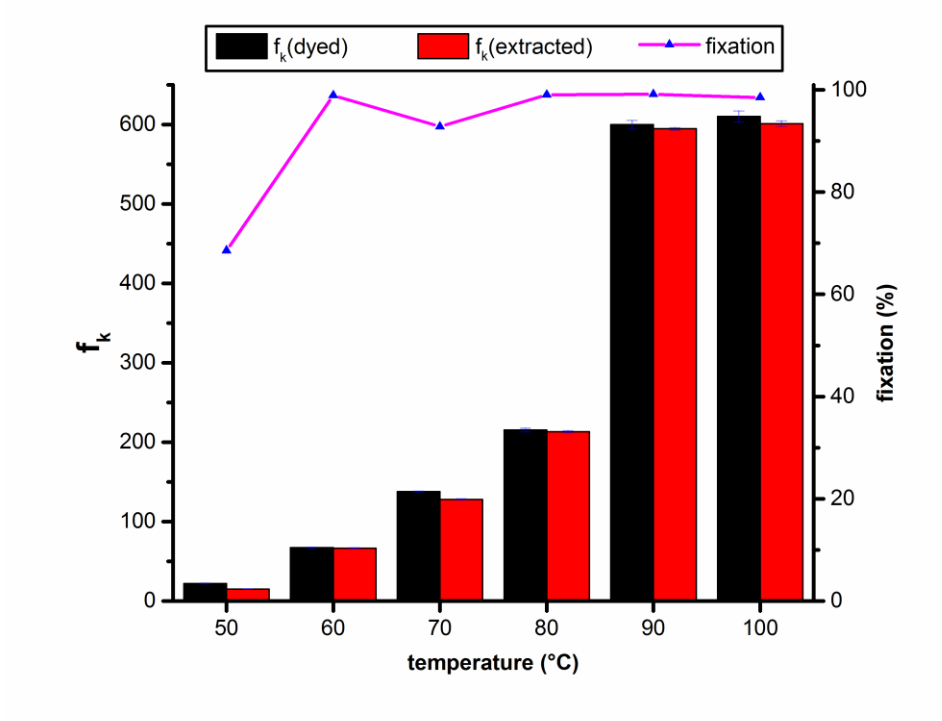


Figure 6.3 Effect of temperature on dye fixation of wool fabric and the f_k value in scCO$_2$ with 5 % owf. of RD 5 and 40 % owf. of pre-treatment water, at 140 bar, during 60 minutes

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6.2.1.3 Investigation of the effect of dyeing time on the dyeing of wool, using RD 5 containing vinyl sulphone

Dyeing times of 60 minutes were first employed with the synthesised RD 5. 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.

As shown in Figure 6.4, increasing the dyeing time significantly enhanced the dyeing qualities. Remarkably, within 20 minutes a $f_{k(dyed)}$ value of 414.7 was already achieved on the dyed piece of wool. A slight improvement was observed after 60 minutes of dyeing time. The strongest 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 ($F > 96$ %) were achieved, but also the fixation rates were independent of dyeing period (after more than 5 minutes dyeing period). Hence, it is likely that the nucleophilic addition reaction between vinyl sulphonyl groups and wool fibre occured within 5 minutes under these dyeing conditions.

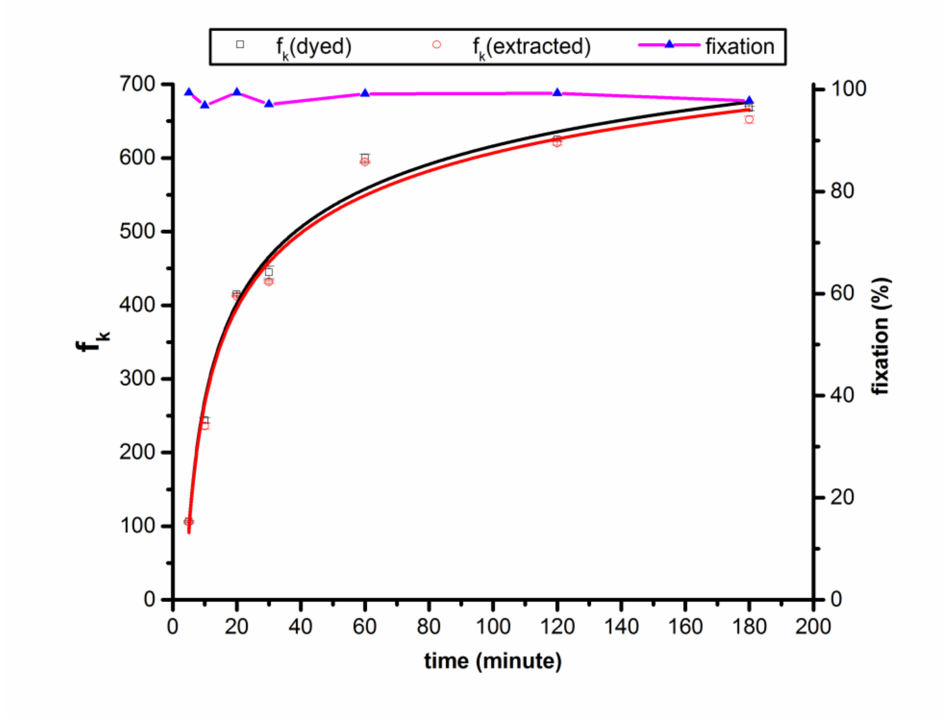


Figure 6.4 Effect of dyeing period on dye fixation of wool fabric and the f_k value dyed in $scCO_2$ with 5 % owf. of RD 5 and 40 % of owf. water in the pre-treatment process at 90 °C, 140 bar

6.2.1.4 Colour fastness test

The wash fastness of wool fabrics coloured with 5 % owf. of dye, 40 % owf. of water, pretreated at 90 °C and 140 bar at various dyeing times was tested (Table 6.1). 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 lower than the fading fastness, especially for samples treated at insufficient dyeing times.

Table 6.1 The fastness data of wool fabrics coloured with 5 % owf of dye, 40% owf. of water in $scCO_2$ at 90 °C, 140 bar during different dyeing period

Dyeing time (mins)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	5	5	5	4-5	5	4-5	5
20	5	5	5	4-5	5	5	5
60	5	5	5	5	5	5	5
180	5	5	5	5	5	5	5

6.2.2 Dyeing cotton fabric using RD 5 containing the vinyl sulphonyl group

6.2.2.1 Investigation of the effect of water pre-treatment on the dyeing of cotton, using the RD 5 containing vinyl sulphone

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

The colour depth (Figure 6.5) increased initially and reached a maximum value [$f_{k(\mathrm{dyed})}$ = 126.3] at 30 % owf. of water addition before decreasing. Moreover, the hydrophobic, synthesised RD 5 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 % owf. of water addition. 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 % owf.

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

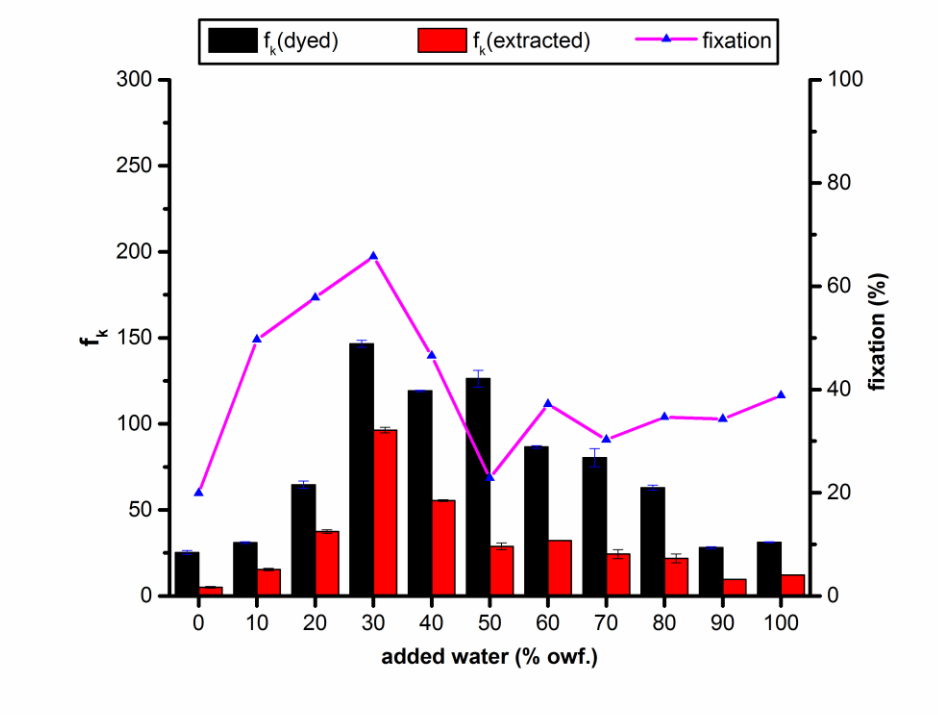


Figure 6.5 Effect of water pre-treatment on cotton fabric on the f_k value and the dye fixation dyed in scCO$_2$ with 5 % owf. of RD 5 at 90 °C, 140 bar for 60 minutes

6.2.2.2 Investigation of the effect of the temperature on the dyeing of cotton, using the RD 5 containing vinyl sulphone

The experimental setup involving scCO$_2$ was designed to operate at 140 bar during a 60 minutes dyeing time. Based on the results of the optimum amount of water addition in 6.2.2, cotton was pre-treated with 30 % owf. of water for 30 minutes before the dyeing experiments were carried out. The results are shown in Figure 6.6.

The f_k value of the dyed cotton remained steady and relatively low until 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 of the fixation, which indicates 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 a dyeing reached a maximum approximately 90 °C.

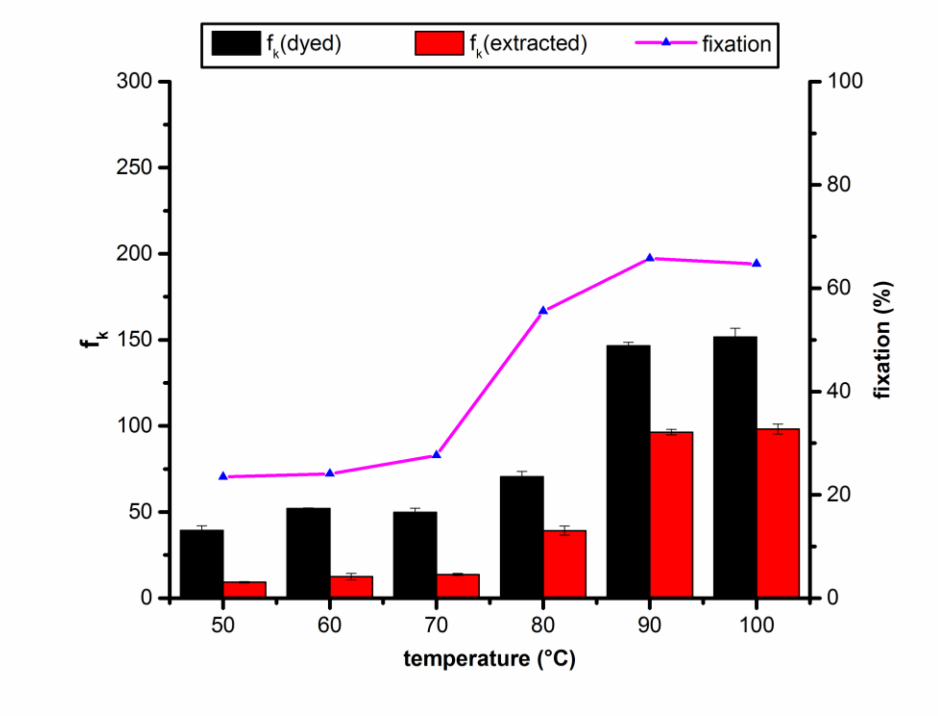


Figure 6.6 Effect of temperature on dye fixation of cotton fabric and the f_k value dyed in $scCO_2$ using 5 % owf. of RD 5 and 30 % owf. of water, at 140 bar, for 60 minutes

6.2.2.3 Investigation of the effect of the dyeing time on the dyeing of cotton, using RD 5 containing vinyl sulphone

In this series of experiments, the dyeing system was maintained at 140 bar, and 90 °C. The cotton fabric was pre-treated with 30 % owf. of water. Figure 6.7 shows the interesting result that the fixation reached 61.7 % after only 30 minutes of dyeing. Moreover, the f_k value increased rapidly to 146.6 within 60 minutes. The dyeing results generally improved with time, indicating that the dyeing completed after around 60 minutes.

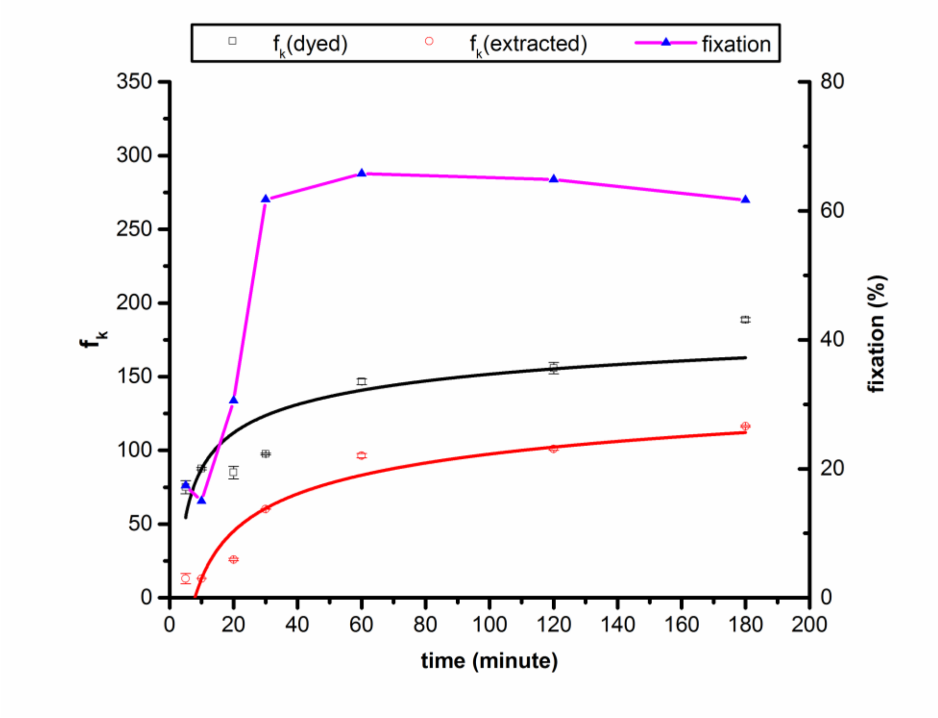


Figure 6.7 Effect of dyeing time on the dyeing of wool fabric with respect to the f_k value and on the dye fixation dyeing in scCO$_2$ with 5 % owf. of RD 5 at 90 °C, 140 bar

6.2.2.4 Colour fastness test

Table 6.2 The fastness data of cotton fabrics coloured with 5 % owf of dye, 30 % owf. of water in scCO$_2$ at 70 °C, 140 bar at different dyeing times

Dyeing time (mins)	Wash fastness						
	Fading	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
10	4	3-4	4	3	3-4	3-4	3
20	5	4	5	4-5	3-4	3-4	4
60	5	5	5	5	5	4-5	5
180	5	5	5	5	5	4-5	5

Table 6.2 summarises the fastness properties of 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 also 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.

6.2.3 Microscopy study

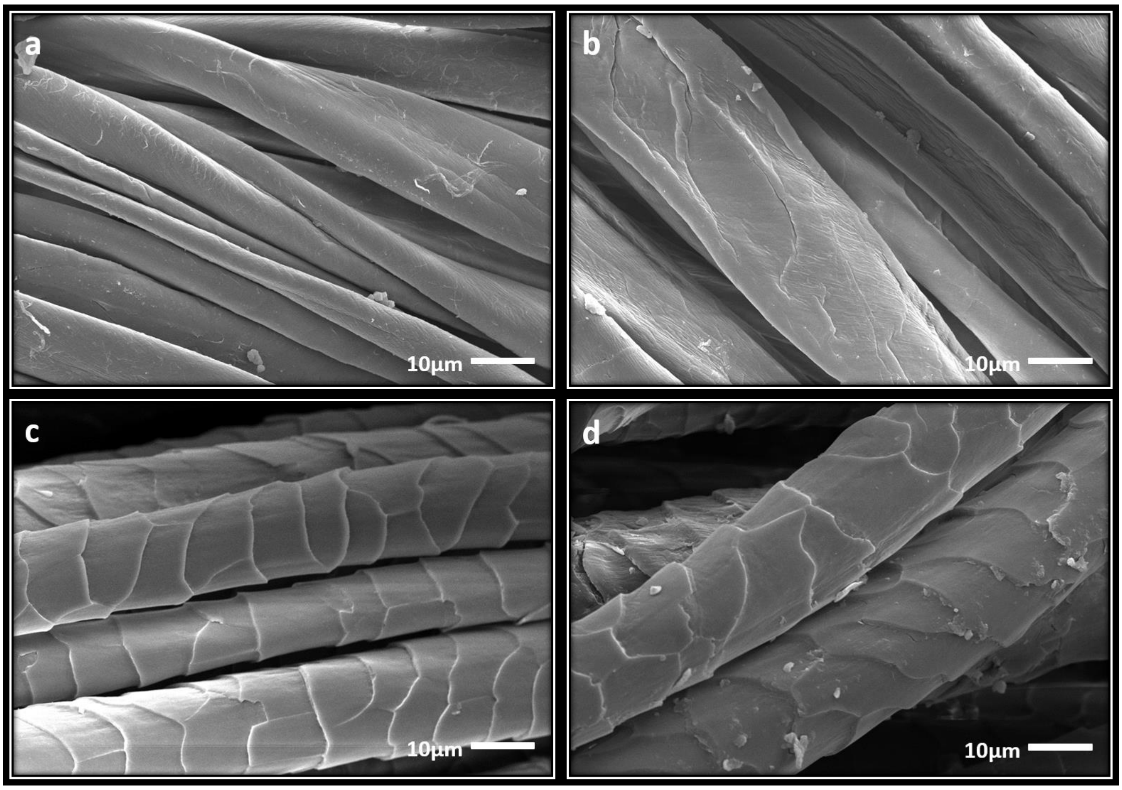


Figure 6.8 SEM images of fabrics. Microscopy studies were undertaken to identify (a) supplied cotton fibres; (b) dyed cotton fibre; (c) supplied wool fibres; (d) dyed wool fibre; Dyed conditions: cotton-90 °C, 140 bar, 3 % owf. of dye, 30 % owf. of water pre-treatment, 60 minutes dyeing time; wool-90 °C, 140 bar, 5 % owf. of dye, 40 % owf. of water pre-treatment, 60 minutes dyeing time

Microscopy studies were undertaken to establish whether or not the process conditions damaged the fibres. Figure 6.8 demonstrates that the control cotton fibres and wool fibres have smooth surfaces. It is apparent that apart from some particles present, no clear split or fibrillation was observed on the surface of either the cotton or the wool fibres after dyeing (Figure 6.8b, 6.8d) compared to the control fibres (Figure 6.8a, 6.8c). 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 [7].

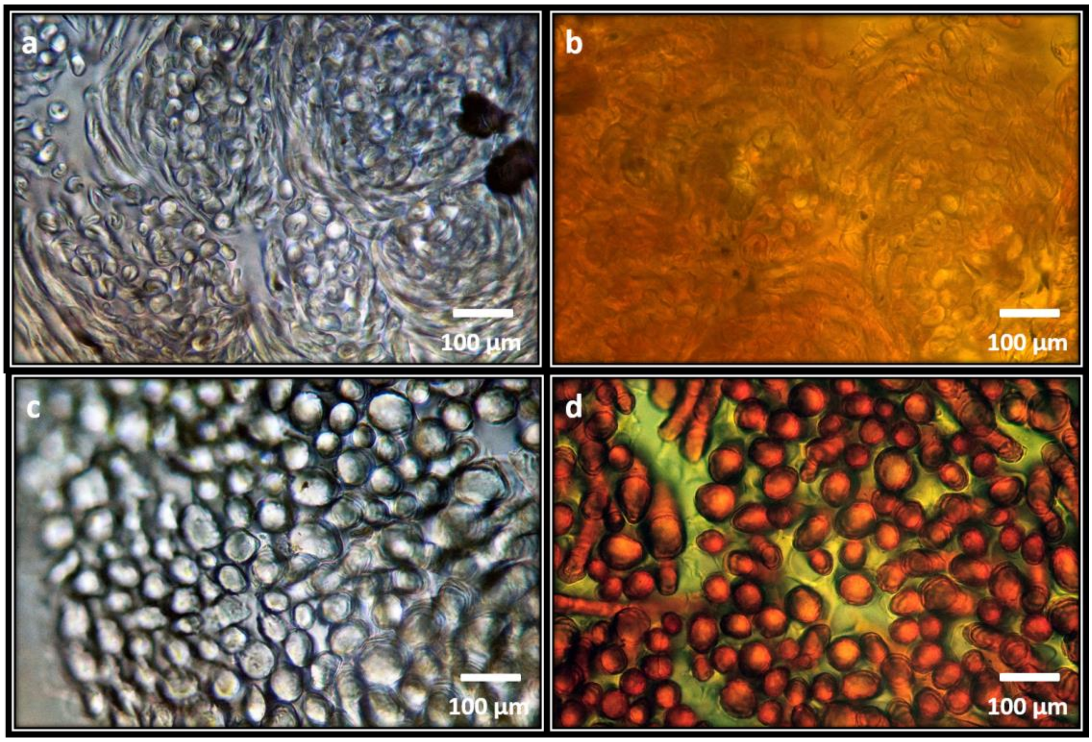


Figure 6.9 Cross-section images (a) supplied cotton fibres; (b) dyed cotton fibre; (c) supplied wool fibres; (d) dyed wool fibre; Dyed conditions: cotton-90 °C, 140 bar, 5 % owf. of dye, 30 % owf. of water pre-treatment, 60 minutes dyeing time; wool-90 °C, 140 bar, 5 % owf. of dye, 40 % owf. of water pre-treatment, 60 minutes dyeing time

Cross-section images of the dyed wool fabrics and the dyed cotton fabrics shows that ring dyeing was not observed, and an effective dye uptake occurred during dyeing in $scCO_2$. Examples are shown in Figure 6.9. The individual wool fibres can be observed to have been well penetrated by the RD 5 molecules. However, there were some lighter areas in Figure 6.9b that indicate that an uneven dyeing occurred for the dyed cotton. The diffusion of dyes in the free volume in amorphous areas is not very fluent due to the hindrance of intramolecular hydrogen bonds of cotton. In order to enhance the levelness of dyeing on the dyed cotton, it will be necessary to improve the dye itself, but also need to modify the dyeing equipment, for instant, improving the circulation of the dyeing process.

6.2.4 Description of dyed samples and visual assessments

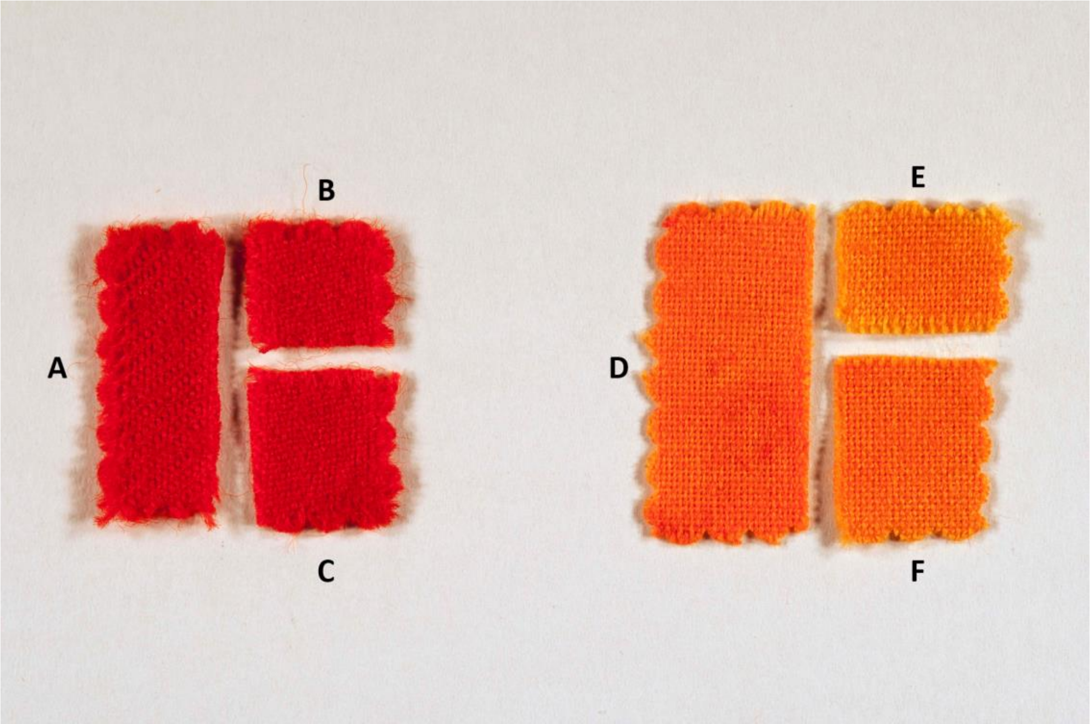


Figure 6.10 Dyed wool and cotton samples using RD 5 in $scCO_2$

Figure 6.10 displays 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.

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

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

The dyed cotton was relatively light orange in colour. The colour of the samples faded after wash and extraction. More colour was lost when the cotton samples were 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.

6.3 Conclusions

A major benefit of using the vinyl sulphonyl group is that the nucleophilic addition reaction between fabric and dyes can be carried out under the acidic condition in the supercritical 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 presented to synthesise a reactive disperse dye containing a vinyl sulphonyl group, starting from a thiol. This is a simple method to add vinyl sulphonyl group to not only an azo dye, but also possibly to other chromophore groups, such as the anthroquinone group. This has the potential to provide modified dyes of a wide range of hues.

Excellent dyeing results including colour depth, fixation and wash fastness for wool were achieved with the synthesised vinyl sulphonyl modified disperse dye. 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 % owf. of water remaining on the fabric after 30 minutes of water pre-treatment. The dyeing of cotton was not as effective as the dyeing of wool under similar dyeing conditions, but still gave an acceptable colour. The colour depth and fixation values were improved by using 30 % owf. 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 textile dyeing purposes, such as the dyeing of curtains.

The dyeing conditions for dyeing both wool and cotton were much milder than those reported in the literature, indicating that there is a potential to try industrial scale experiments with this dyeing method [4, 5, 11, 13-15].

Overall, the synthesised vinyl sulphonyl disperse dyes are considered to be the most suitable dyes for natural fabric dyeing in supercritical carbon dioxide. The dyeing also only requires a small quantity of water, with no other additional component required.

6.4 References

1. Bach, E., E. Cleve, and E. Schollmeyer, *Past, present and future of supercritical fluid dyeing technology–an overview*. Review of Progress in Coloration and Related Topics, 2002. **32**(1): p. 88-102.
2. Lewis, D., *The dyeing of wool with reactive dyes.* Journal of the Society of Dyers and Colourists, 1982. **98**(5-6): p. 165-175.
3. van der Kraan, M., M.V. Fernandez Cid, G.F. Woerlee, W.J.T. Veugelers, and G.J. Witkamp, *Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes.* The Journal of Supercritical Fluids, 2007. **40**(3): p. 470-476.
4. Long, J.-J., Y.-Q. Ma, and J.-P. Zhao, *Investigations on the level dyeing of fabrics in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2011. **57**(1): p. 80-86.
5. Liao, S., Y. Ho, and P. Chang, *Dyeing of nylon 66 with a disperse ‑reactive dye using supercritical carbon dioxide as the transport medium.* Coloration Technology, 2000. **116**(12): p. 403-407.
6. Group, Y., *DryDye™ Fabrics – Exclusively from the Yeh Group* (online). Accessed 02/02/2017. ; Available from: http://www.knittingindustry.com/uploads/1090/drydye-tech-paper-wol.pdf.
7. Banchero, M., *Supercritical fluid dyeing of synthetic and natural textiles - a review.* Coloration Technology, 2013. **129**(1): p. 2-17.
8. Abou Elmaaty, T. and E. Abd El-Aziz, *Supercritical carbon dioxide as a green media in textile dyeing: A review.* Textile Research Journal, 2017: p. 0040517517697639.
9. Liao, S.-K., P.-S. Chang, and Y.-C. Lin, *Dyeing of Polypropylene Fibers with Disperse Dyes by Supercritical Carbon Dioxide.* Journal of Textile Engineering, 2000. **46**(4): p. 123-129.
10. Liao, S.-K. and P.-S. Chang, *Special Issue-Supercritical Fluids Literatures on Dyeing Technique of Supercritical Fluid Carbon Dioxide.* American Journal of Analytical Chemistry, 2012. **3**(12): p. 8.
11. Long, J.-J., G.-D. Xiao, H.-M. Xu, L. Wang, C.-L. Cui, J. Liu, M.-Y. Yang, K. Wang, C. Chen, and Y.-M. Ren, *Dyeing of cotton fabric with a reactive disperse dye in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2012. **69**: p. 13-20.
12. Choi, Y.-S. and S. Nešić, *Corrosion behavior of carbon steel in supercritical* CO_2*-water environments.* Corrosion 2009, 2009.
13. Fernandez Cid, M.V., J. van Spronsen, M. van der Kraan, W.J.T. Veugelers, G.F. Woerlee, and G.J. Witkamp, *Excellent dye fixation on cotton dyed in supercritical carbon dioxide using fluorotriazine reactive dyes.* Green Chemistry, 2005. **7**(8): p. 609.
14. Gao, D., H.-S. Cui, T.-T. Huang, D.-F. Yang, and J.-X. Lin, *Synthesis of reactive disperse dyes containing halogenated acetamide group for dyeing cotton fabric in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2014. **86**: p. 108-114.
15. Yang, D.-F., X.-J. Kong, D. Gao, H.-S. Cui, T.-T. Huang, and J.-x. Lin, *Dyeing of cotton fabric with reactive disperse dye contain acyl fluoride group in supercritical carbon dioxide.* Dyes and Pigments, 2017. **139**: p. 566-574.

Chapter 7 Characterisation of synthesised disperse reactive dyes

^{1}H and spectra were measured on a Bruker UltraShield 300 MHz spectrometer using an internal deuterium lock. ^{13}C NMR were measured on a Bruker UltraShield 75 MHz NMR instrument. Chemical shifts are reported in parts per million (ppm) downfield from and coupling constants are given in Herts (Hz). Tetramethylsilane (TMS) is defined as 0 ppm for ^{1}H NMR spectra. When describing ^{1}H NMR data, the following abbreviations are used; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer and the samples were analysed as neat. Positive electron impact (EI+) analysis was run on a Waters GCT Premier spectrometer. Positive and negative electrospray ionisation was performed on a Bruker Daltronics microTOF spectrometer. Thin layer chromatography (TLC) was carried out on Merck pre-coated glass silica gel 60 F_{254} plates with fluorescent indicator 254 nm, and were visualised using ultraviolet light. A Varian 50 Probe UV-Visible Spectrometer was used for analysis of the dye synthesised. The absorption spectrum was recorded between 300-700 nm, to determine the wavelength of maximum absorption.

7.1 Characterisation of RD 1

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.1): δ 8.398-8.380 (d, J = 5.4, 2H), 8.037-8.019 (d, J = 5.4, 2H), 7.976-7.959 (d, J = 5.1, 2H), 7.274-7.258 (d, J = 4.8, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.2): δ (ppm) 155.705, 151.363, 150.020, 125.804, 125.099, 125.042, 124.914, 123.623, 123.401; ν_{max}/cm^{-1} (ATR) (Figure 7.3): 2253, 1768, 1735, 1598, 1517, 1341; m/z (ESI): found 269.1 (M+1); $C_{13}H_8N_4O_3$ requires 268.06 (M+1).

The strong and broad peak at 2253 cm^{-1} was assigned to the isocyanate reactive group (N=C=O) stretching vibration. The weak peak at 3439 cm^{-1} suggests that there was few unreacted amine molecules present in the final product. The UV/Vis spectrum shown in Figure 7.4 indicated that the dye exhibits a maximum absorption at 435 nm.

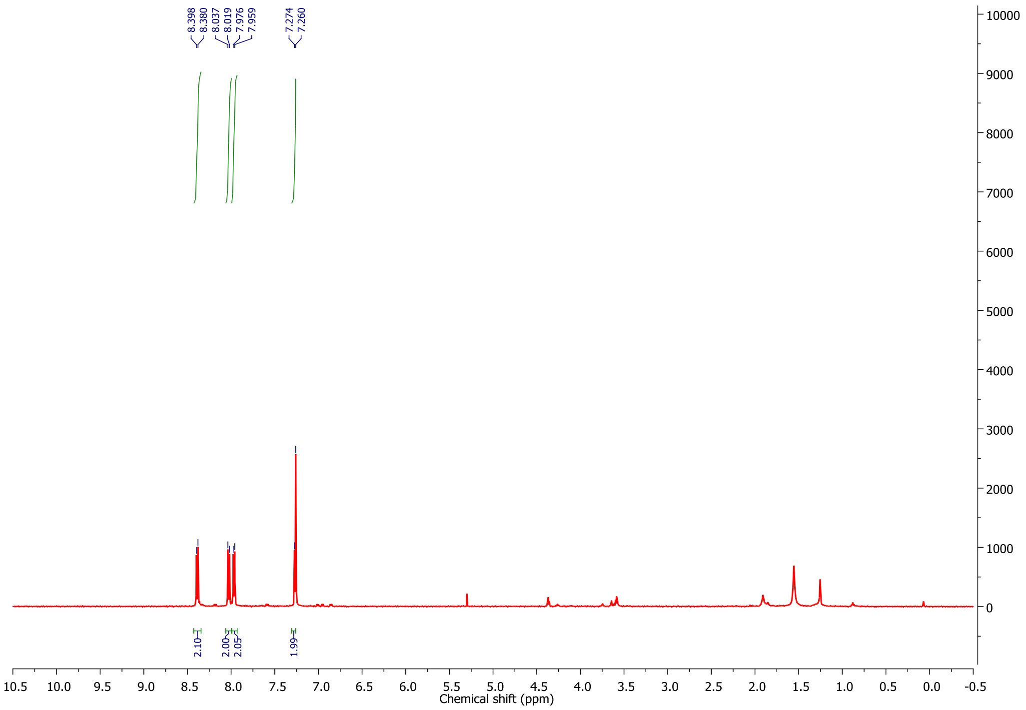


Figure 7.1 ^{1}H NMR spectrum of RD 1

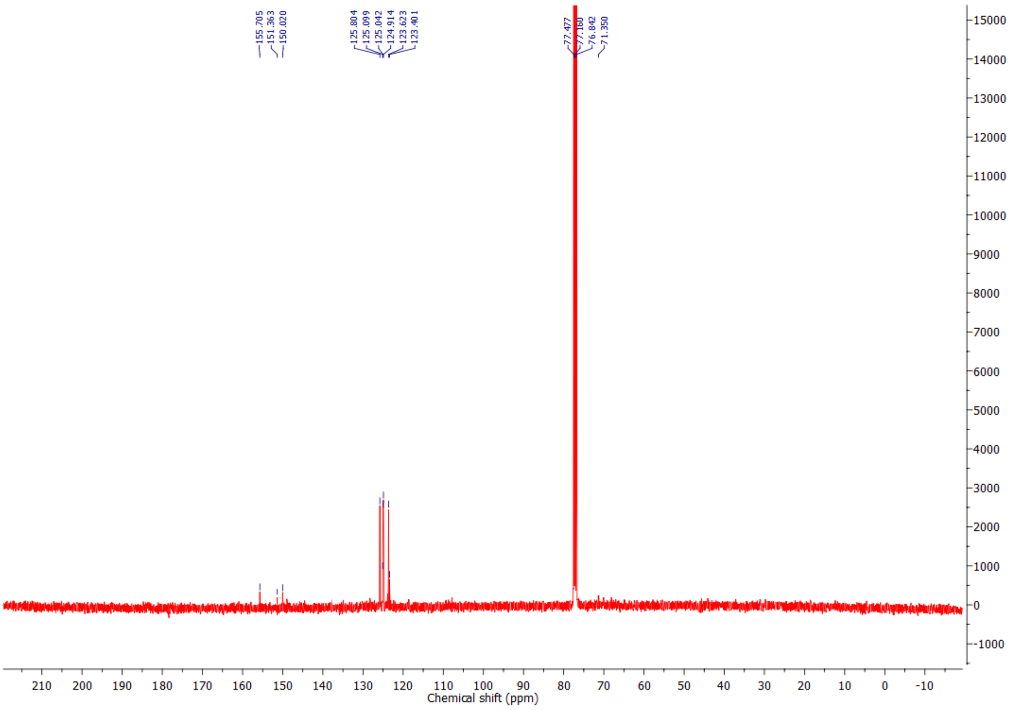


Figure 7.2 ^{13}C NMR spectrum of RD 1

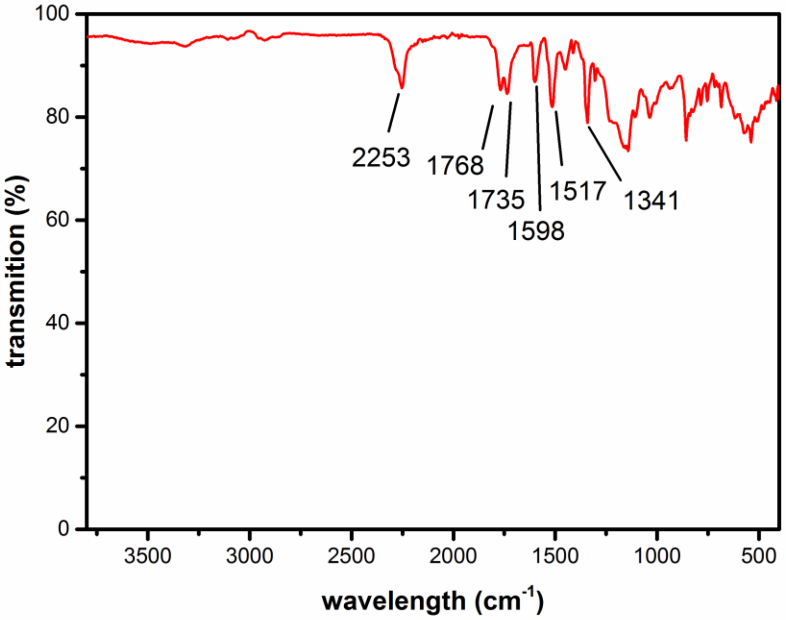


Figure 7.3 FTIR spectrum of RD 1

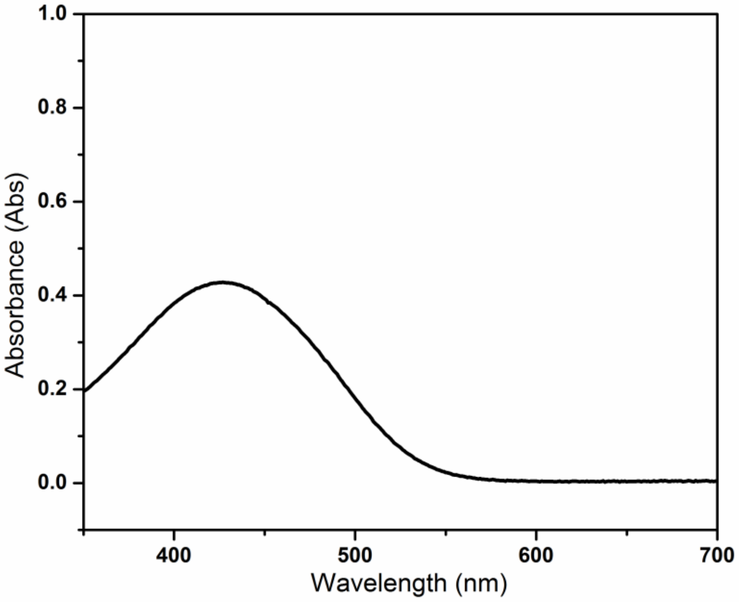


Figure 7.4 UV-vis spectrum of the RD 1

7.2 Characterisation of RD 2

7.2.1 Characterisation of 2-methyl-4-[2-(4-nitrophenyl) diazenyl] benzenamine

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.5): δ 8.345-8.327 (dd, *J* = 5.4, 2H), 7.947-7.930 (d, *J* = 5.1, 2H), 7.790(s, 1H), 7.760-7.743 (d, *J* = 5.4, 1H), 4.216 (s, 2H), 2.608-2.562 (q, *J* = 13.8, 2H), 1.562 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.6): δ (ppm) 156.750, 148.490, 147.813, 146.019, 132.279, 124.809, 123.201, 122.999, 122.905, 115.522, 27.922, 22.155; ν_{max}/cm^{-1} (ATR) (Figure 7.7): 3439, 3315, 3197, 2966, 1740, 1640, 1602, 1510, 1439. 1341; m/z (ESI): found 271.23 (M+1); $C_{14}H_{14}N_4O_2$ requires 271.11 (M+1).

The absorption bands at 3315 and 3157 cm^{-1} were attributed to the NH_2 asymmetric and symmetric stretching vibrations respectively. The absorption peak at 2966 cm^{-1} was related to the aromatic C-H stretching vibration.

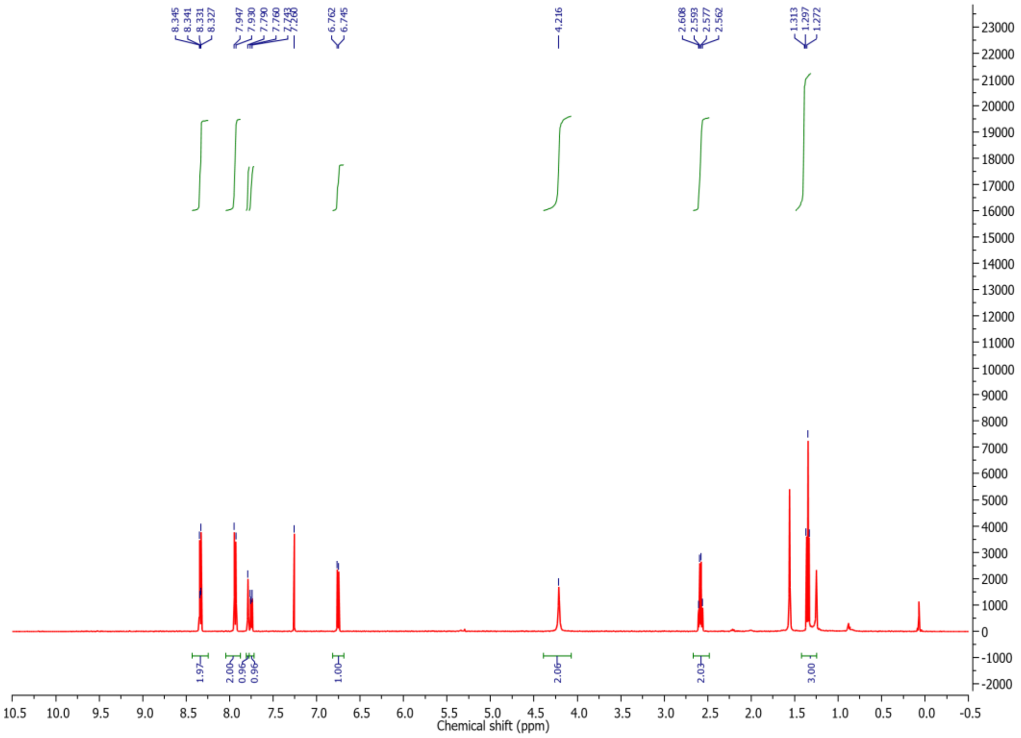


Figure 7.5 ^{1}H NMR spectrum of 2-methyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine

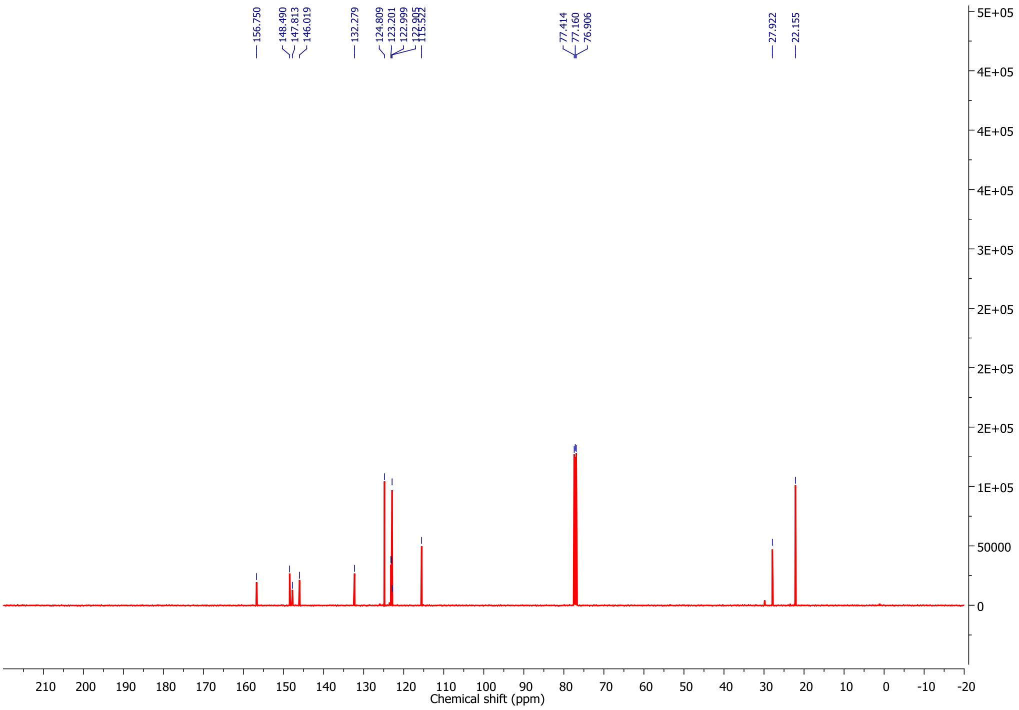


Figure 7.6 ^{13}C NMR spectrum of 2-methyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine

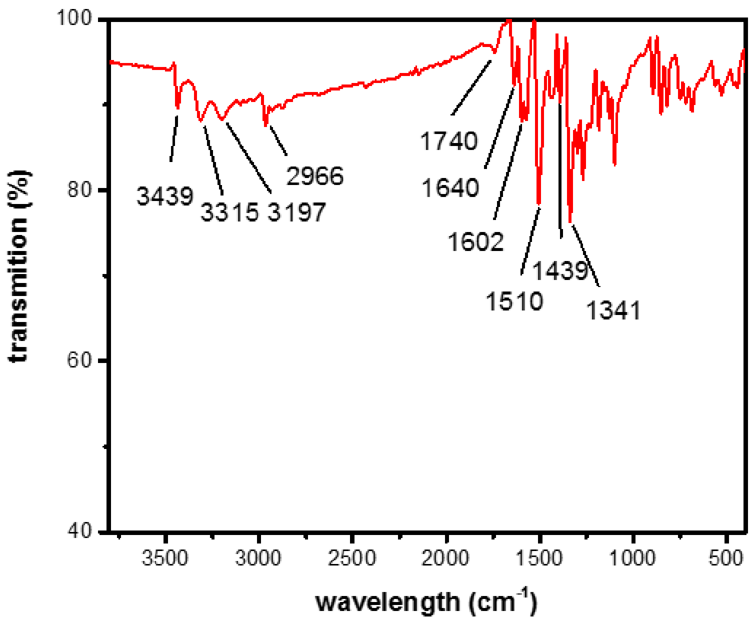


Figure 7.7 FTIR spectrum of 2-methyl-4-[2-(4-nitrophenyl) diazenyl]benzenamine

7.2.2 Characterisation of RD 2

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.8): δ 8.392-8.376 (d, *J* = 4.8, 2H), 8.029-8.014 (d, *J* = 4.5, 2H), 7.868(s, 1H), 7.813-7.796 (d, *J* = 5.1, 1H), 2.815-2.771 (q, *J* = 13.2, 2H), 1.331 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.9): δ (ppm) 155.840, 150.420, 148.878, 144.019, 135.267, 126.958, 125.613, 124.898, 123.554, 122.618, 121.531, 29.564, 22.800; ν_{max}/cm^{-1} (ATR) (Figure 7.10): 2968, 2276, 1772, 1738, 1538, 1462, 1340; m/z (ESI): found 297.31 (M+1); $C_{15}H_{12}N_4O_3$ requires 297.09 (M+1).

The absorption bands at 2968 and 2932 cm^{-1} were attributed to the alkane C-H stretching vibrations. The strong and broad peak at 2276 cm^{-1} was assigned to the isocyanate reactive group (N=C=O) stretching vibration. The peak at 3439 cm^{-1} suggests that there were some unreacted amine molecules present in the final product. The UV/Vis spectrum shown in Figure 7.11 indicated that the dye exhibits a maximum absorption at 360 nm.

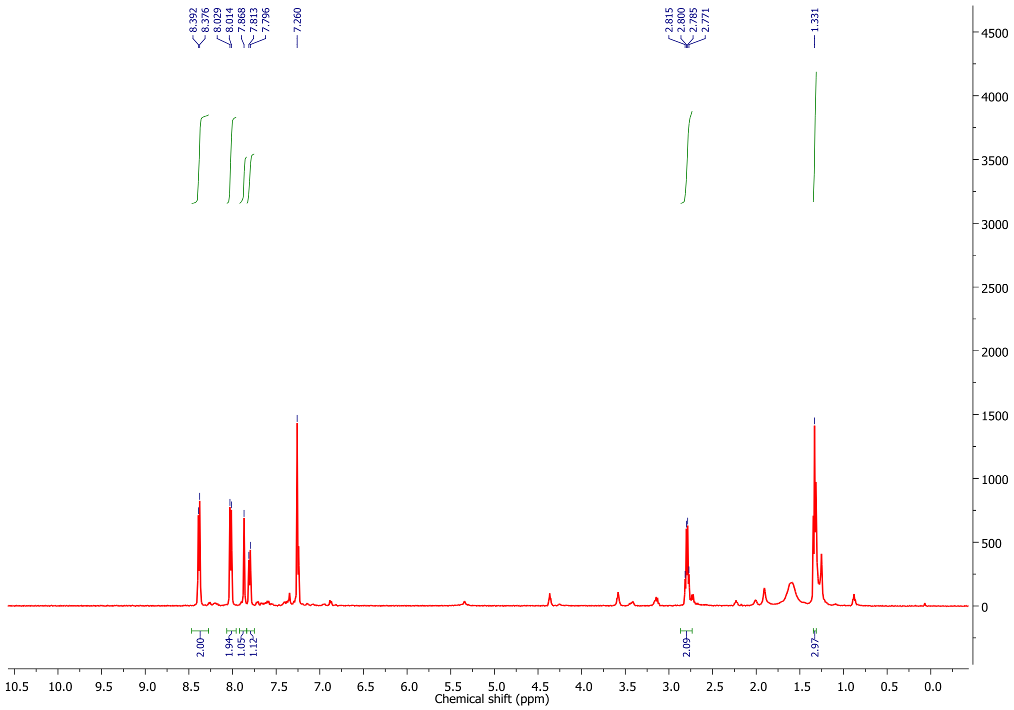


Figure 7.8 ^{1}H NMR spectrum of RD 2

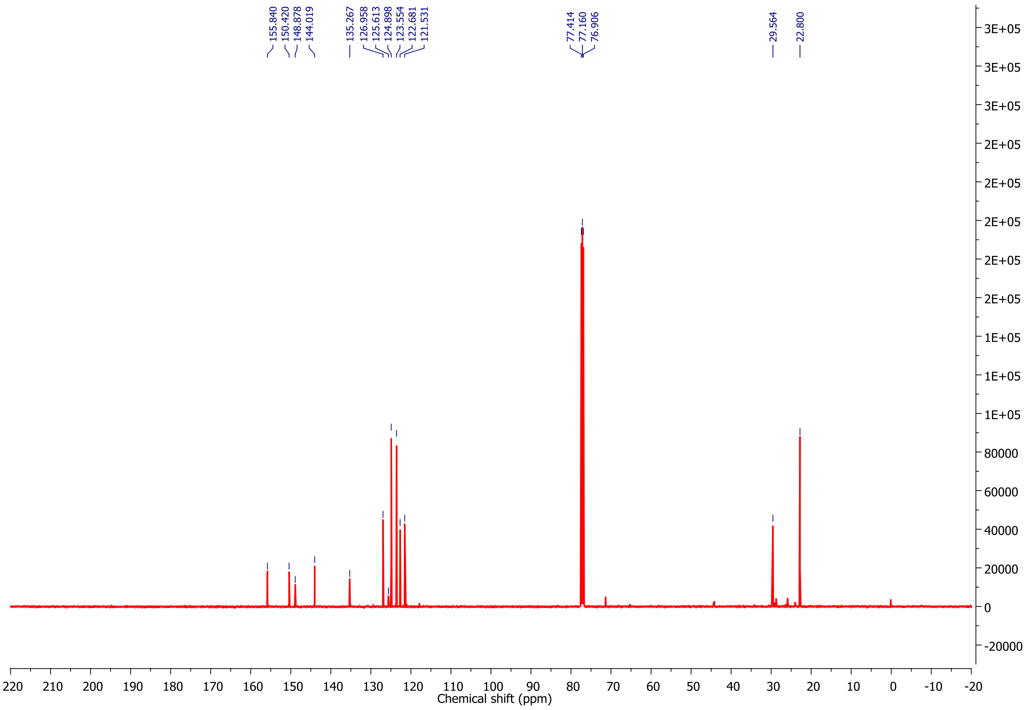


Figure 7.9 ^{13}C NMR spectrum of RD 2

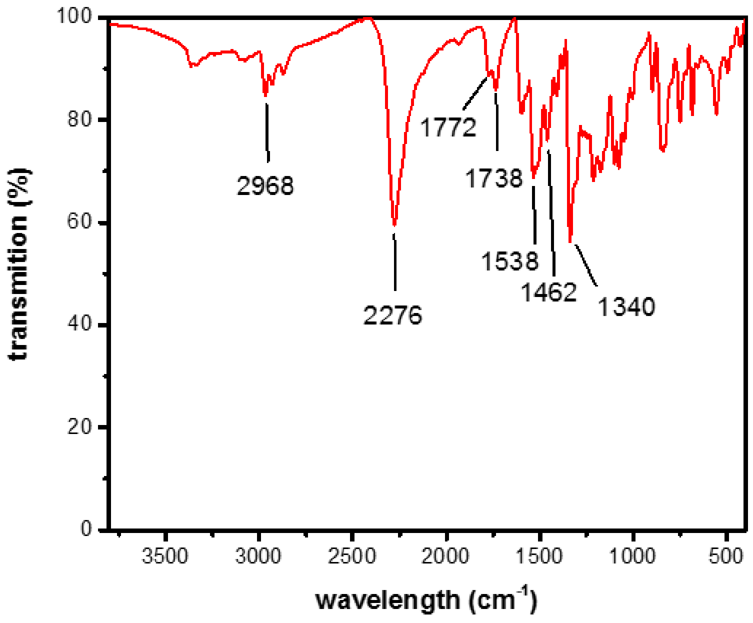


Figure 7.10 FTIR spectrum of RD 2

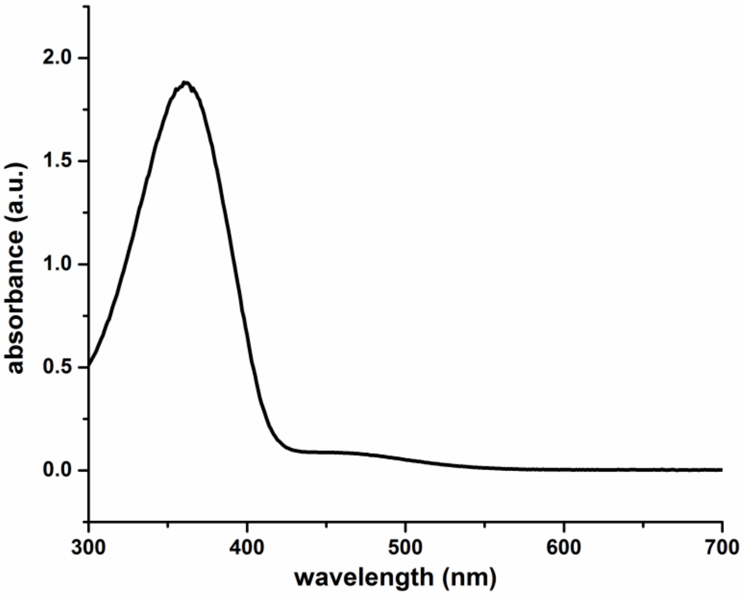


Figure 7.11 UV-vis spectrum of the RD 2

7.3 Characterisation of RD 3

7.3.1 Characterisation of 2-isopropyl-4-[2-(4-nitrophenyl)diazenyl] benzenamine

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.12): δ 8.340-8.322 (dd, *J* = 5.4, 2H), 7.947-7.929 (dd, *J* = 5.4, 2H), 7.862-7.858(d, *J* = 1.2, 1H), 7.734-7.717 (d, *J* = 5.1, 1H), 4.262 (s, 1H), 2.926-2.872 (m, *J* = 16.2, 1H), 1.359-1.345 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.13): δ (ppm) 156.742, 149.103, 147.861, 145.899, 127.731, 124.836, 124.588, 124.298, 122.920, 114.961, 29.845, 23.907, 12.676; ν_{max}/cm^{-1} (ATR) (Figure 7.14): 3483, 3401, 2949, 2865, 1618, 1511, 1447, 1421, 1328; m/z (ESI): found 285.10 (M+1); $C_{15}H_{16}N_4O_2$ requires 285.13 (M+1).

The absorption bands at 3483 and 3401 cm^{-1} were attributed to the NH_2 asymmetric and symmetric stretching vibrations respectively. The absorption bands at 2949 and 2869 cm^{-1} were assigned to the alkane C-H stretching vibrations.

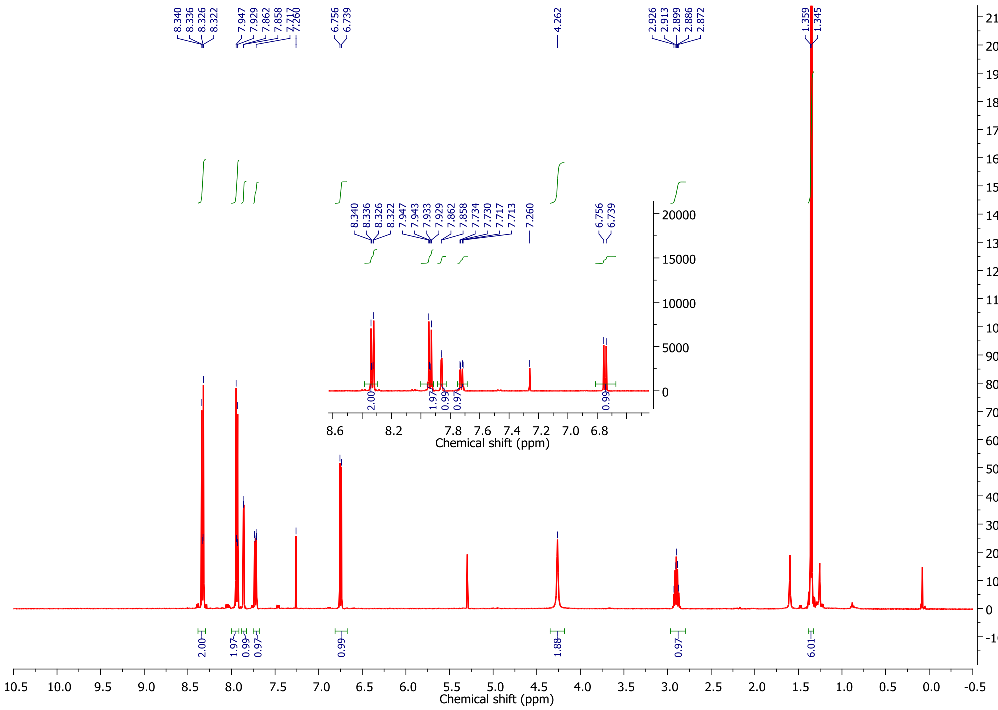


Figure 7.12 ^{1}H NMR spectrum of 2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

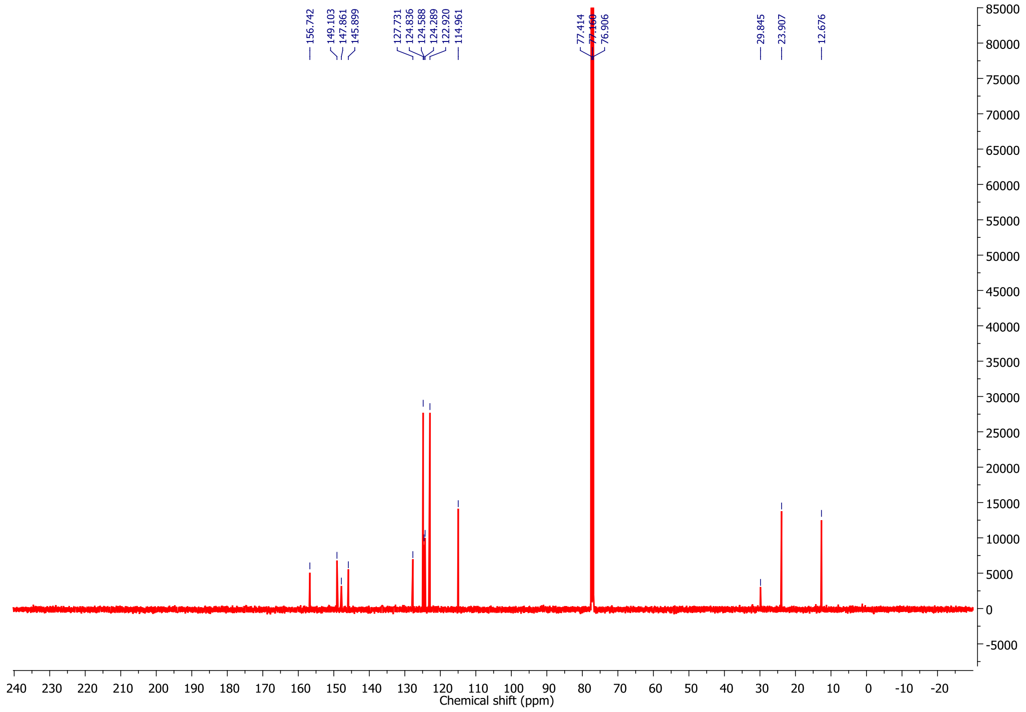


Figure 7.13 ^{13}C NMR spectrum of 2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

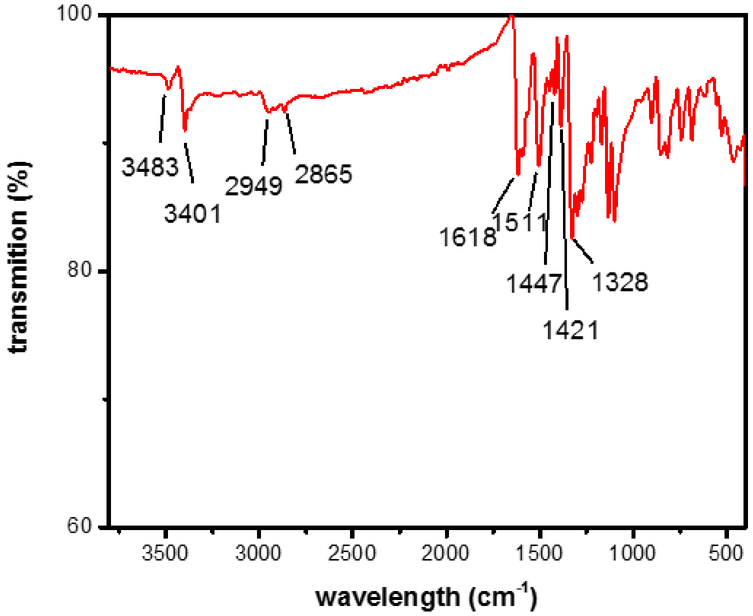


Figure 7.14 FTIR spectrum of 2-isopropyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

7.3.2 Characterisation of RD 3

^{1}H NMR (300 MHz, CDCl$_3$) (Figure 7.15): δ 8.395-8.377 (dd, *J* = 5.4, 2H), 8.038-8.020 (dd, *J* = 5.4, 2H), 7.934-7.930 (d, *J* = 1.2, 1H), 7.797-7.776 (d, *J* = 6.3, 1H), 7.265-7.223 (q, *J* = 12.6, 1H), 3.335-3.280 (m, *J* = 16.5, 1H), 1.346-1.332 (d, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) (Figure 7.16): δ (ppm) 156.738, 149.100, 147.722, 145.690, 127.727, 124.840, 124.579, 124.295, 122.922, 122.192, 114.956, 29.914, 23.908, 12.675; ν_{max}/cm^{-1} (ATR) (Figure 7.17): 2964, 2930, 2869, 2279, 1775, 1739, 1540, 1453, 1342; m/z (ESI): found 311.013 (M+1); $C_{16}H_{14}N_4O_3$ requires 311.11 (M+1).

The absorption peaks at 2964, 2930 and 2869 cm^{-1} were attributed to the alkane C-H stretching vibrations. The strong and broad absorption band at 2279 cm^{-1} was characteristic of the isocyanate reactive group (N=C=O) stretching vibration. The small peak at 3367 cm^{-1} suggests that there were some unreacted amine molecules present in the final product. The UV/Vis spectrum in Figure 7.18 indicated that the dye exhibits a maximum absorption at 361 nm.

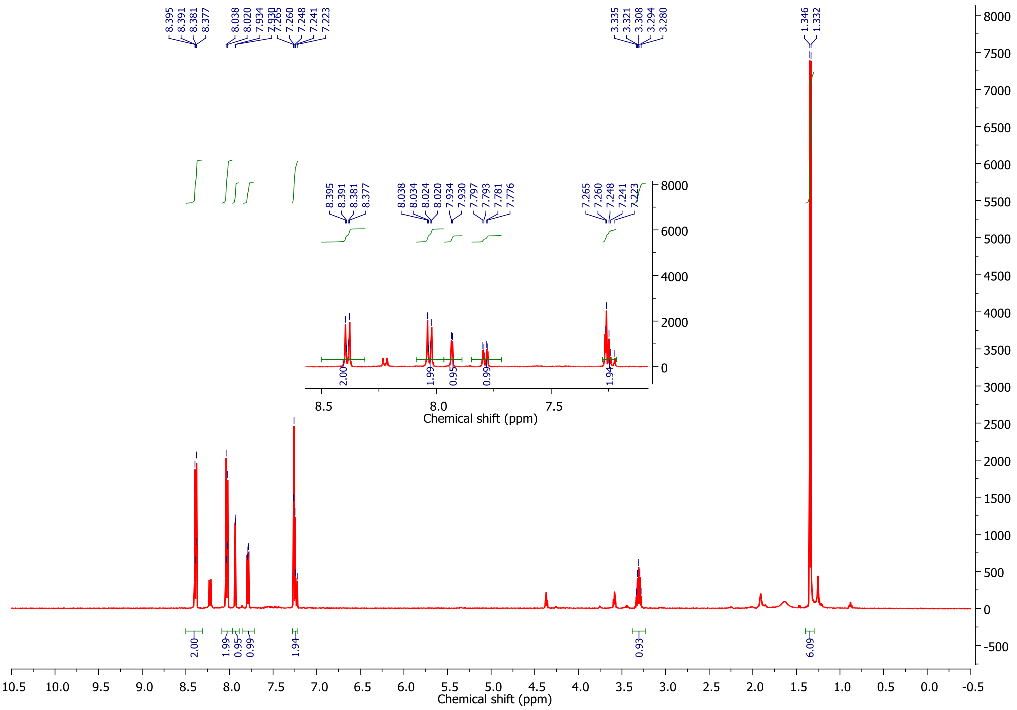


Figure 7.15 ^{1}H NMR spectrum of RD 3

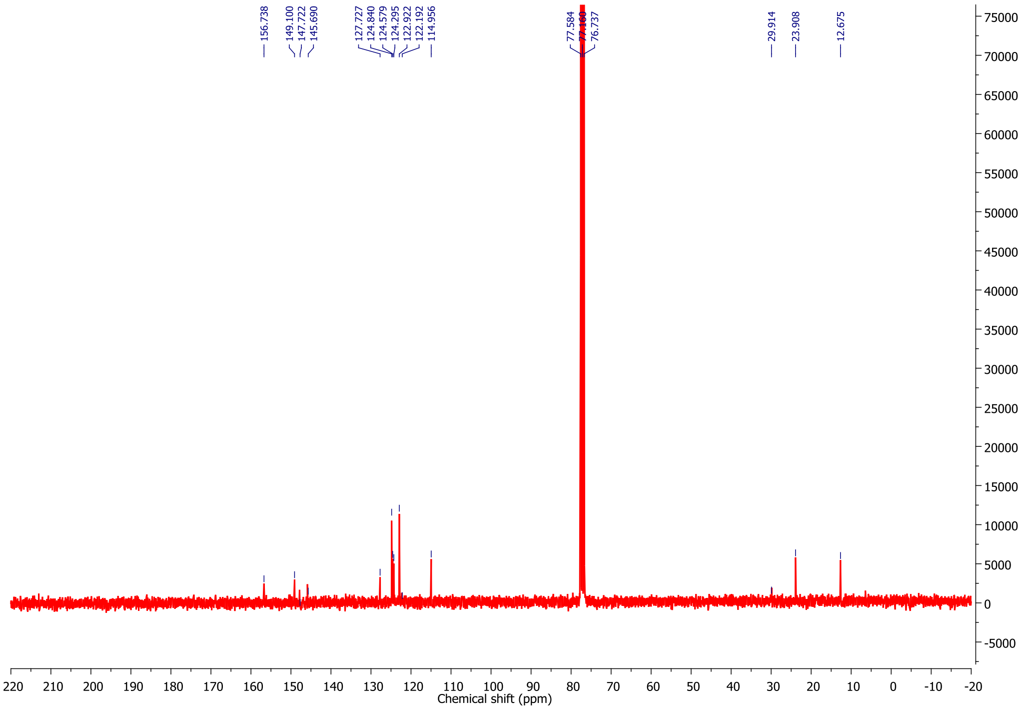


Figure 7.16 ^{13}C NMR spectrum of RD 3

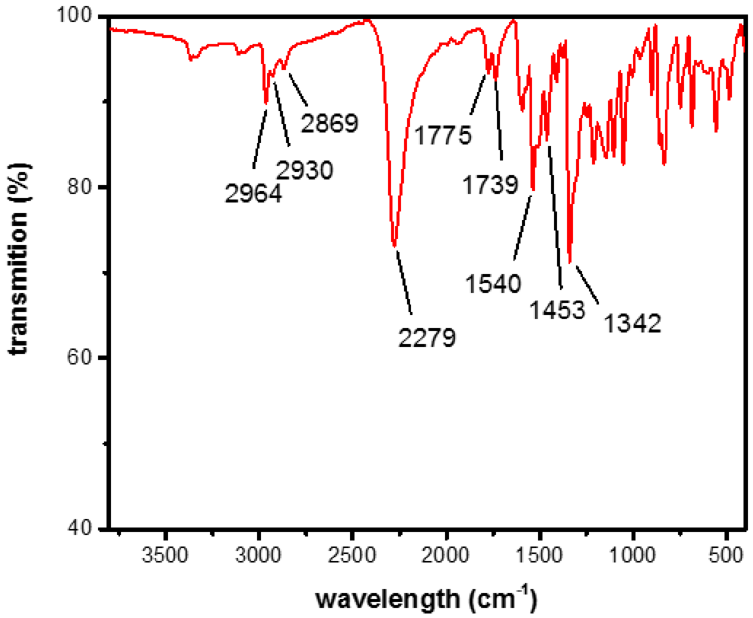


Figure 7.17 FTIR spectrum of RD 3

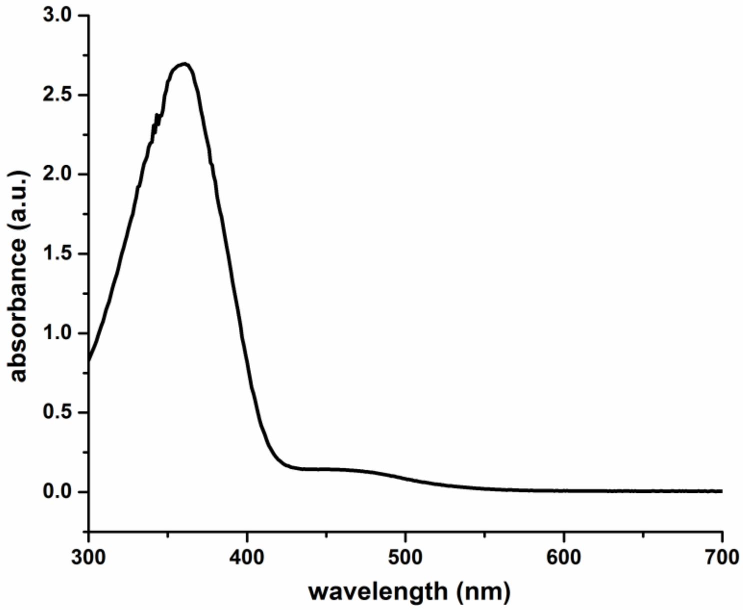


Figure 7.18 UV-vis spectrum of the RD 3

7.4 Characterisation of RD 4

7.4.1 Characterisation of 2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl] benzenamine

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.19): δ 8.350-8.332 (dd, *J* = 5.4, 2H), 7.976-7.972 (d, *J* = 1.2, 1H), 7.952-7.934 (d, *J* = 5.4, 2H), 7.745-7.724 (d, *J* = 6.3, 1H), 6.721-6.704 (d, *J* = 5.1, 1H), 4.448 (s, 1H), 1.501 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.20): δ (ppm) 156.789, 149.566, 147.804, 145.764, 133.285, 125.515, 124.821, 122.894, 122.382, 117.588, 34.434, 29.644; ν_{max}/cm^{-1} (ATR) (Figure 7.21): 3529, 3425, 2965, 2912, 2871, 1617, 1478, 1416, 1380, 1324; m/z (ESI): found 299.68 (M+1); $C_{16}H_{16}N_4O_2$ requires 299.14 (M+1).

The absorption bands at 3529 and 3425 cm^{-1} were attributed to the NH_2 asymmetric and symmetric stretching vibrations respectively. The absorption peak at 2965 was assigned to the alkane C-H stretching vibration.

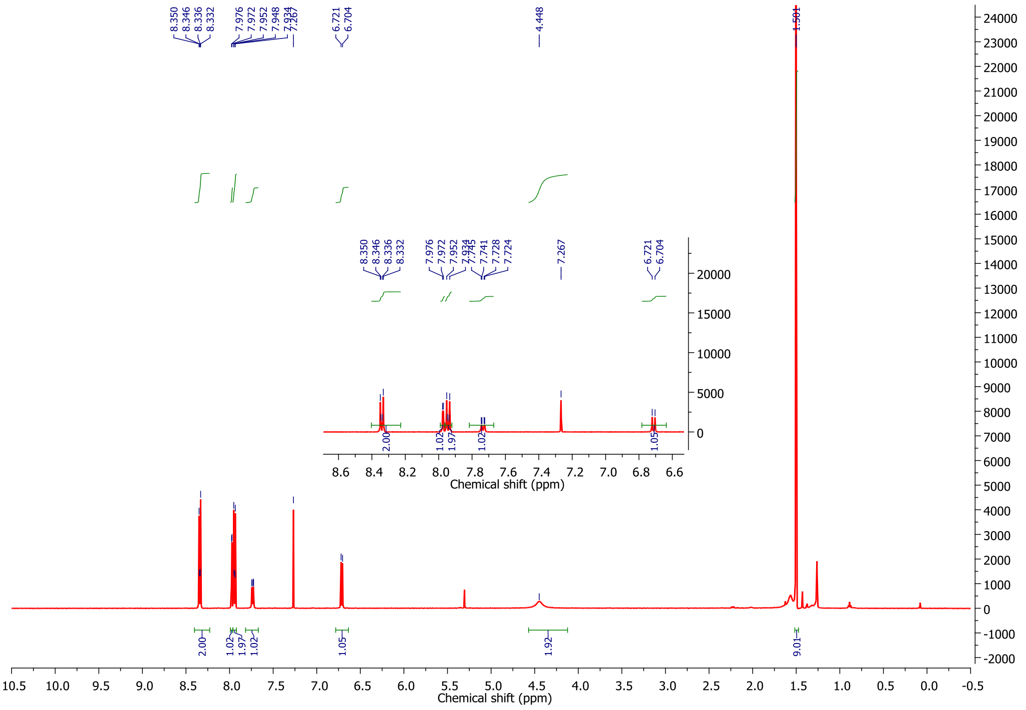


Figure 7.19 ^{1}H NMR spectrum of 2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

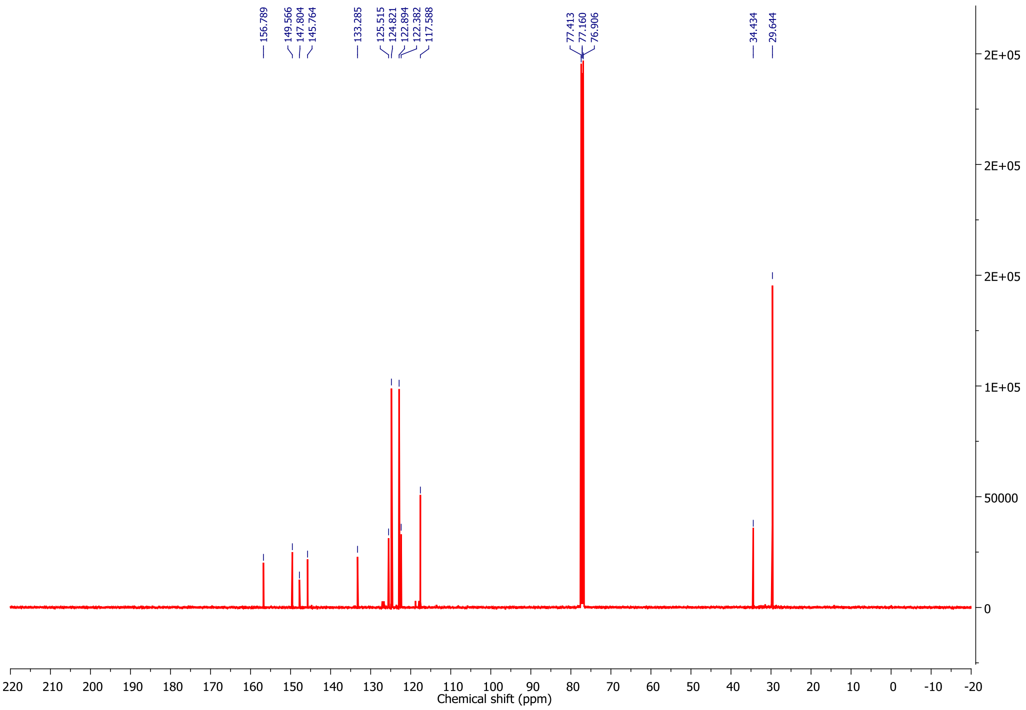


Figure 7.20 ^{13}C NMR spectrum of 2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

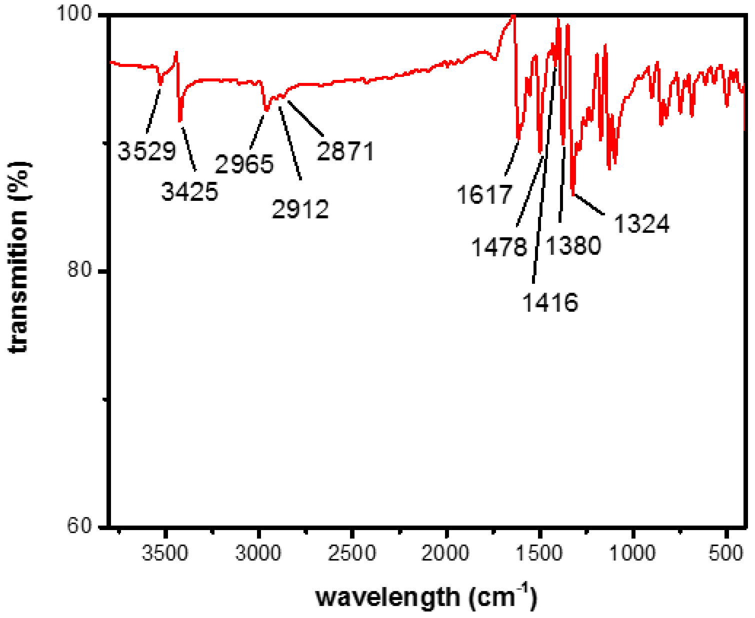


Figure 7.21 FTIR spectrum of 2-tert-butyl-4-[2-(4-nitrophenyl)diazenyl]benzenamine

7.4.2 Characterisation of RD 4

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.22): δ 8.394-8.376 (d, *J* = 5.4, 2H), 8.050-8.045 (d, *J* = 1.5, 1H), 8.034-8.017 (d, *J* = 5.1, 2H), 7.804-7.783 (dd, *J* = 6.3, 1H), 7.269-7.252 (d, *J* = 5.1, 1H), 1.505 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) (Figure 7.23): δ (ppm) 153.342, 149.144, 147.197, 145.842, 143.829, 133.113, 130.059, 125.701, 122.021, 120.819, 118.321, 117.566, 35.287, 34.364, 31.185, 29.602; ν_{max}/cm^{-1} (ATR) (Figure 7.24): 2956, 2917, 2869, 2255, 1775, 1739, 1528, 1466, 1343; m/z (ESI): found 324.38 (M+1); $C_{17}H_{16}N_4O_3$ requires 324.12 (M+1).

The absorption peaks at 2956, 2917 and 2869 cm^{-1} were attributed to the alkane C-H stretching vibrations. The strong and broad adsorption band at 2255 cm^{-1} was assigned as the isocyanate reactive group (N=C=O) stretching vibration. The UV/Vis spectrum in Figure 7.25 indicated that the dye exhibits a maximum absorption at 362 nm.

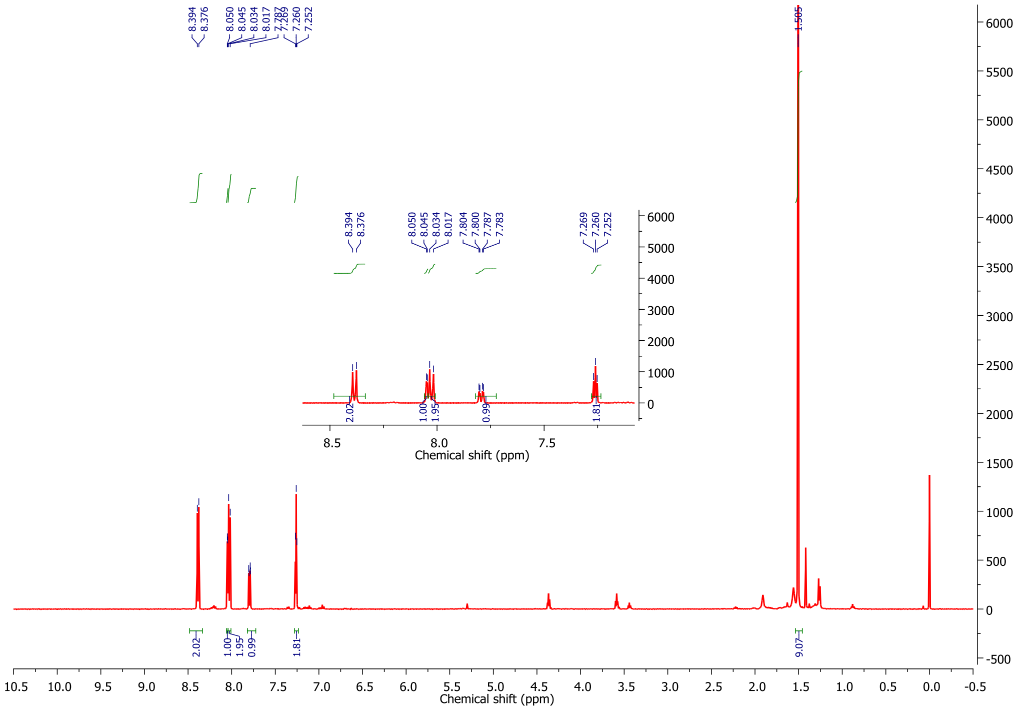


Figure 7.22 ^{1}H NMR spectrum of RD 4

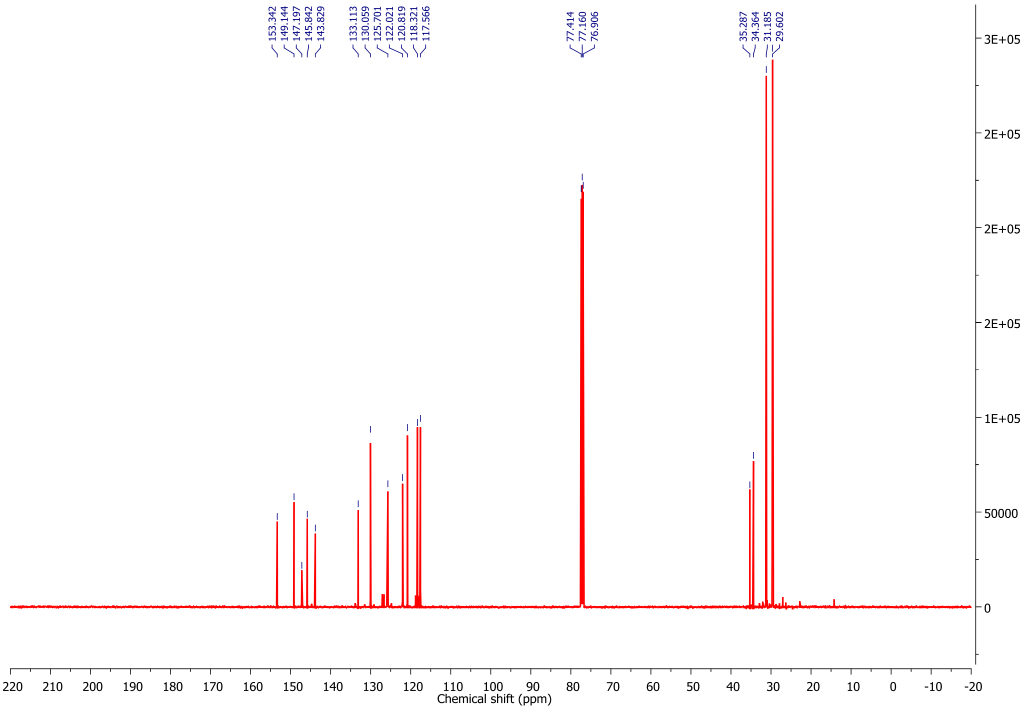


Figure 7.23 ^{13}C NMR spectrum of RD 4

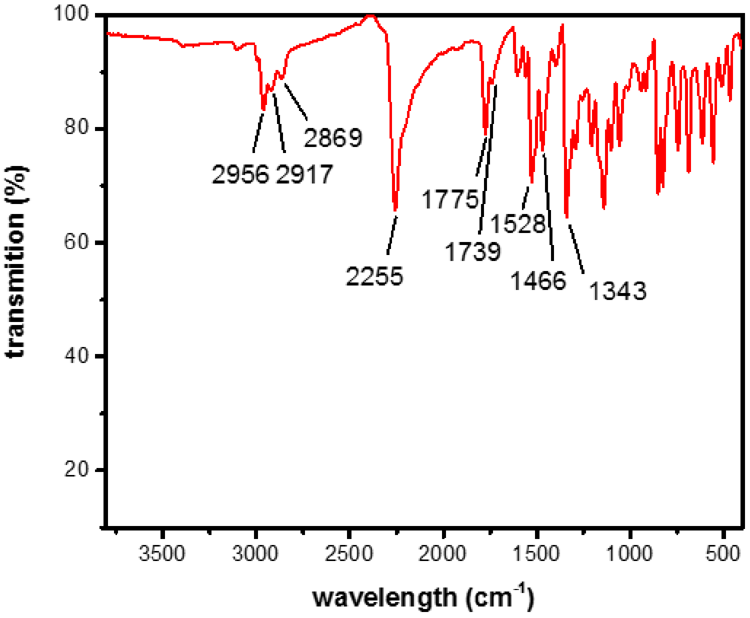


Figure 7.24 FTIR spectrum of RD 4

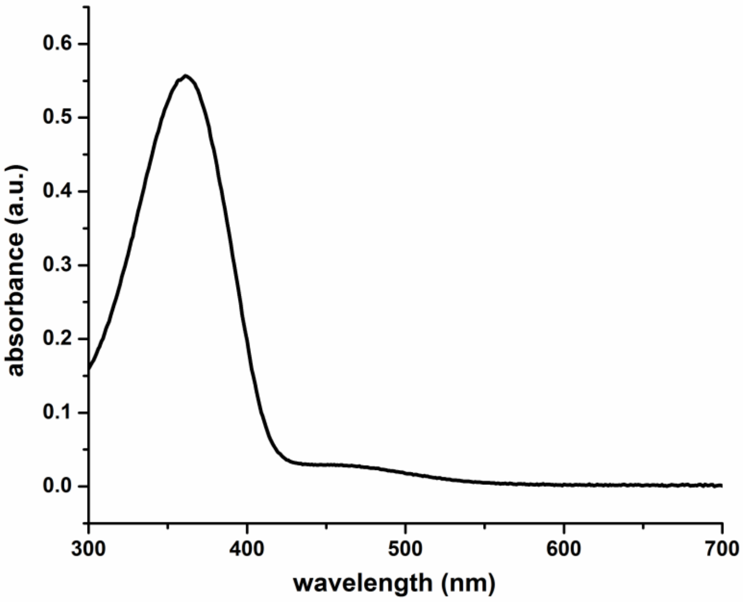


Figure 7.25 UV-vis spectrum of the RD 4

7.5 Characterisation of RD 5

7.5.1 Characterisation of 2-[(4-aminophenyl)sulphanyl]ethanol

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.26): δ 7.272-7.255 (d, *J* = 5.1, 2H), 6.624-6.607 (d, *J* = 5.1, 2H), 3.747(s, 1H), 3.659-3.636 (t, *J* = 6.9, 2H), 2.946-2.922 (t, *J* = 7.2, 2H); C NMR (75 MHz, $CDCl_3$) (Figure 7.27): δ (ppm) 146.611, 134.878, 121.506, 115.777, 60.095, 39.995; ν_{max}/cm^{-1} (ATR) (Figure 7.28): 3342, 3234, 3026, 2919, 2874, 1620, 1494, 1277; m/z (ESI): found 170.0618 (M+1); $C_8H_{11}NOS$ requires 170.0640 (M+1).

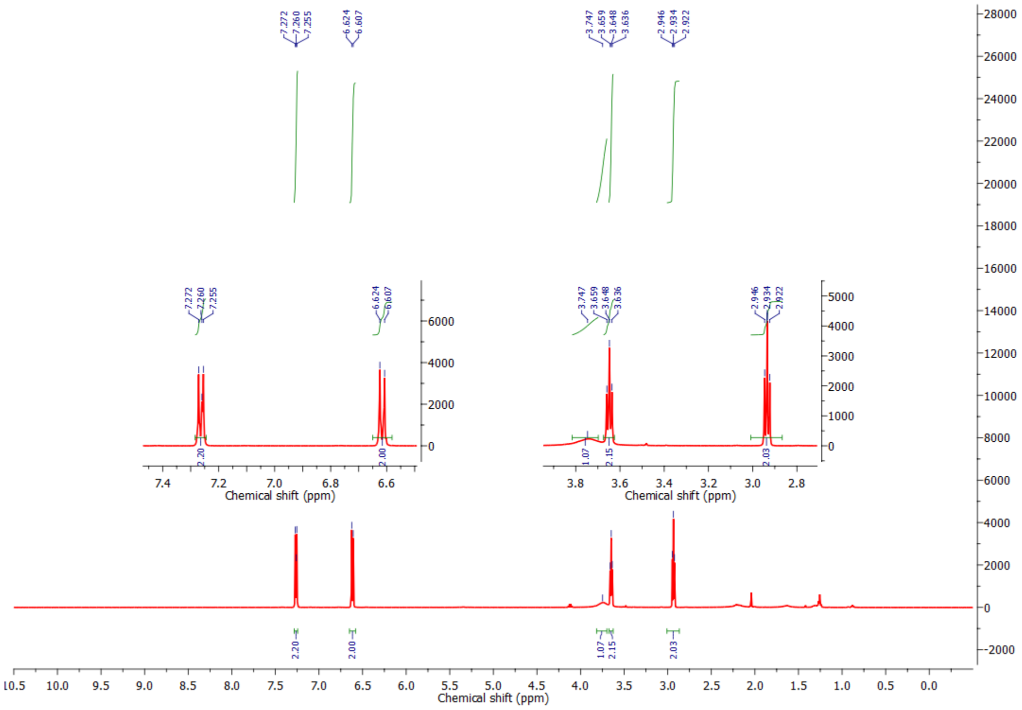


Figure 7.26 ^{1}H NMR spectrum of 2-[(4-Aminophenyl)sulphanyl]ethanol

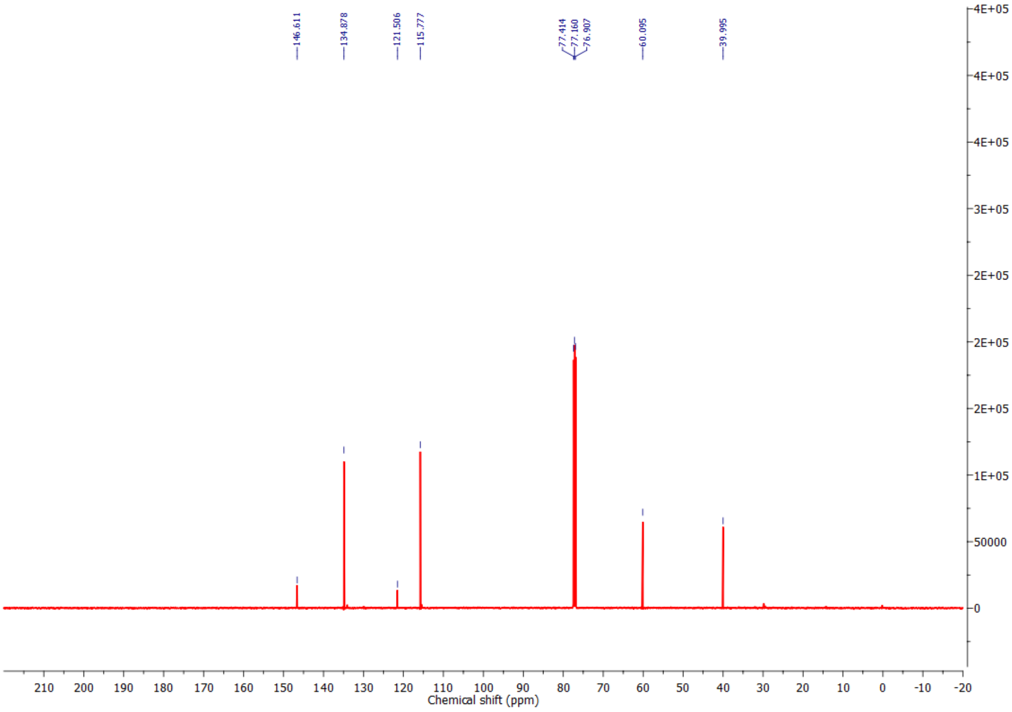


Figure 7.27 ^{13}C NMR spectrum of 2-[(4-Aminophenyl)sulphanyl]ethanol

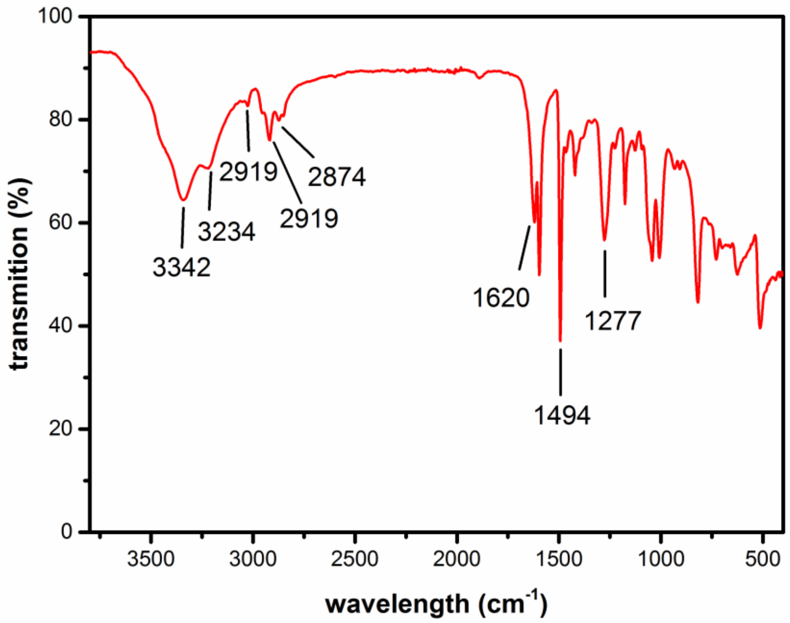


Figure 7.28 FTIR spectrum of 2-[(4-Aminophenyl)sulphanyl]ethanol

7.5.2 Characterisation of N, N-diethyl-4-[((4-sulphanylethanol) phenyl)azo]aniline

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.29): δ 7.845-7.827 (d, *J* = 5.4, 2H), 7.772-7.755 (d, *J* = 5.1, 2H), 7.455-7.438 (d, *J* = 5.1 2H), 6.728-6.709 (d, *J* = 5.7, 2H), 3.812-3.779 (q, *J* = 9.9, 2H), 3.477-3.449 (q, *J* = 12.9, 4H), 3.188-3.164 (t, *J* = 7.2, 2H), 2.040 (s, 1H), 1.570 (s, 4H), 1.246-1.217 (t, *J* = 8.7, 6H); C NMR (75 MHz, $CDCl_3$) (Figure 7.30): δ (ppm) 152.0, 150.4, 143.3, 136.3, 130.1, 125.5, 122.9, 111.2, 60.5, 44.9, 37.2, 12.8; ν_{max}/cm^{-1} (ATR) (Figure 7.31): 3438, 3330, 2971, 2901, 1472, 1266, 634; m/z (ESI): found 330.1652 (M+1); $C_{18}H_{23}N_3OS$ requires 330.1640 (M+1).

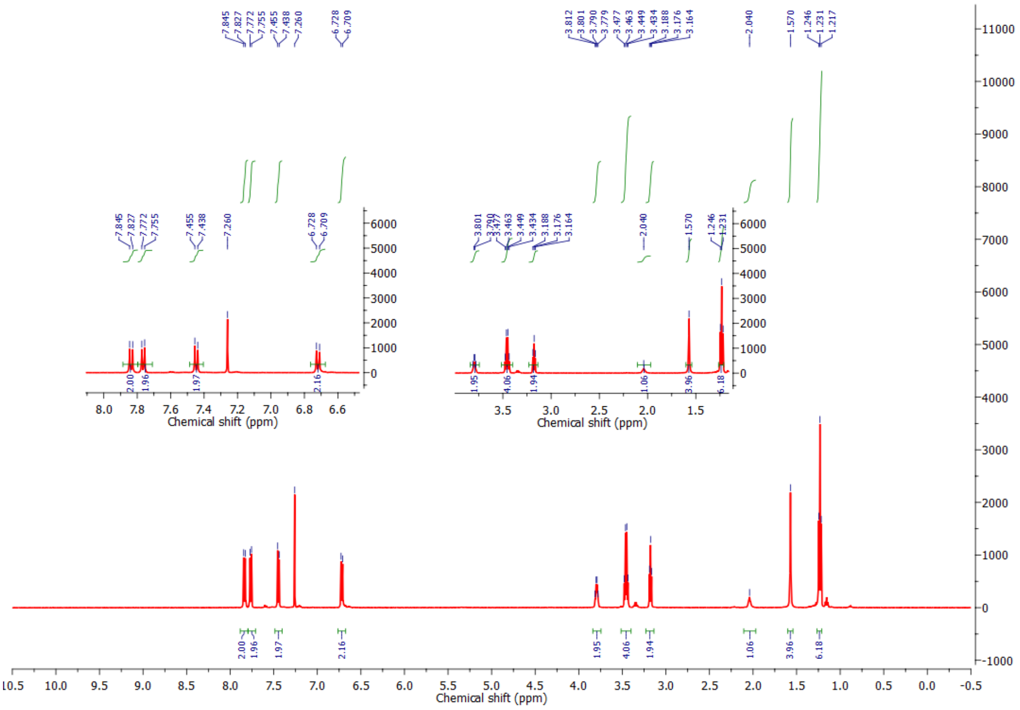


Figure 7.29 ^{1}H NMR spectrum of N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo]aniline

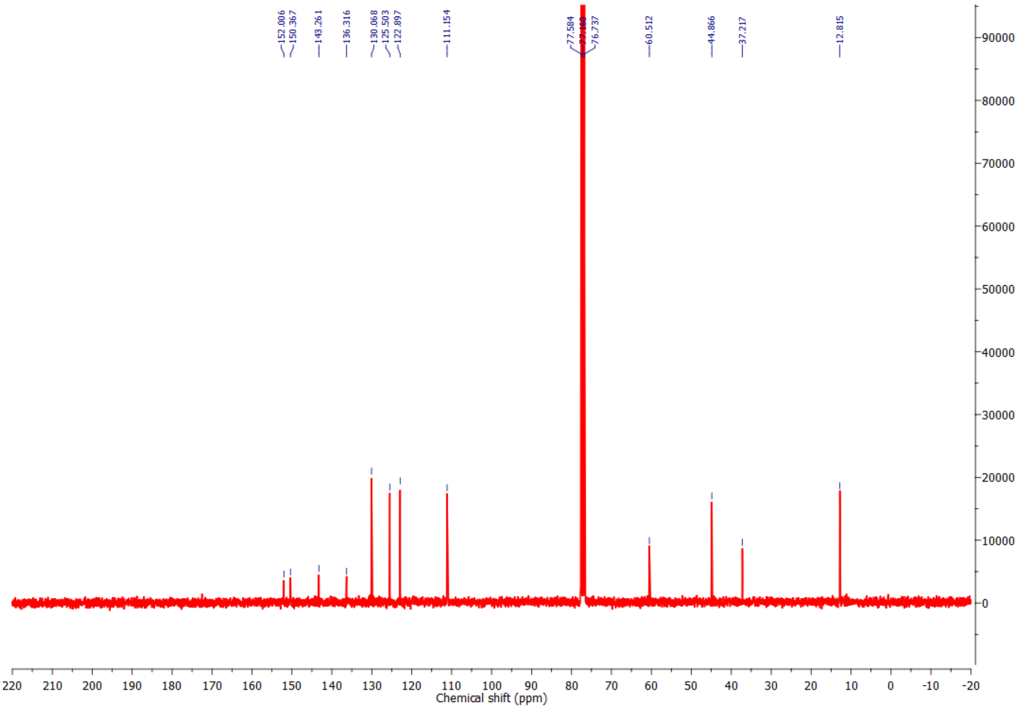


Figure 7.30 ^{13}C NMR spectrum of N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo]aniline

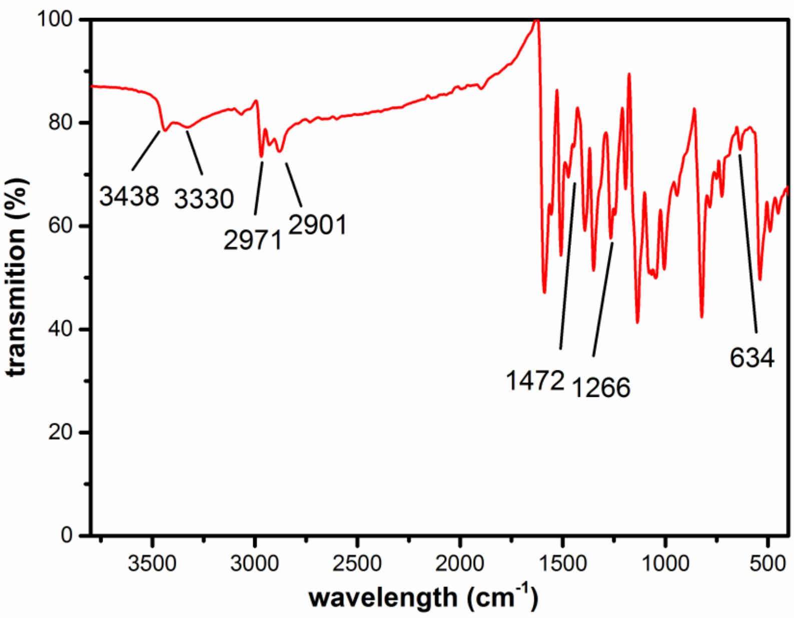


Figure 7.31 FTIR spectrum of N, N-diethyl-4-[((4-sulphanylethanol)phenyl)azo]aniline

7.5.3 Characterisation of N, N-diethyl-4-[(E)-((4-sulphonylethanol) phenyl)azo]aniline

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.32): δ 8.010-7.988 (d, *J* = 6.6, 2H), 7.961-7.939 (d, *J* = 6.6, 2H), 7.893-7.870 (d, *J* = 6.9, 2H), 6.739-6.715 (d, *J* = 7.2, 2H), 4.029-4.002 (t, *J* = 8.1, 2H), 3.501-3.448 (q, *J* = 15.9, 4H), 3.391-3.364 (t, *J* = 8.1, 2H), 1.262-1.227 (t, *J* = 10.5, 6H); C NMR (75 MHz, $CDCl_3$) (Figure 7.33): δ 156.7, 151.1, 143.1, 137.7, 129.0, 126.3, 122.7, 111.0, 58.4, 56.4, 44.8, 12.6; ν_{max}/cm^{-1} (ATR) (Figure 7.34): 3347, 2971, 2928, 1447, 1348, 1270, 1125; m/z (ESI): found 362.1637 (M+1); $C_{19}H_{25}N_3O_2S$ requires 362.1667 (M+1).

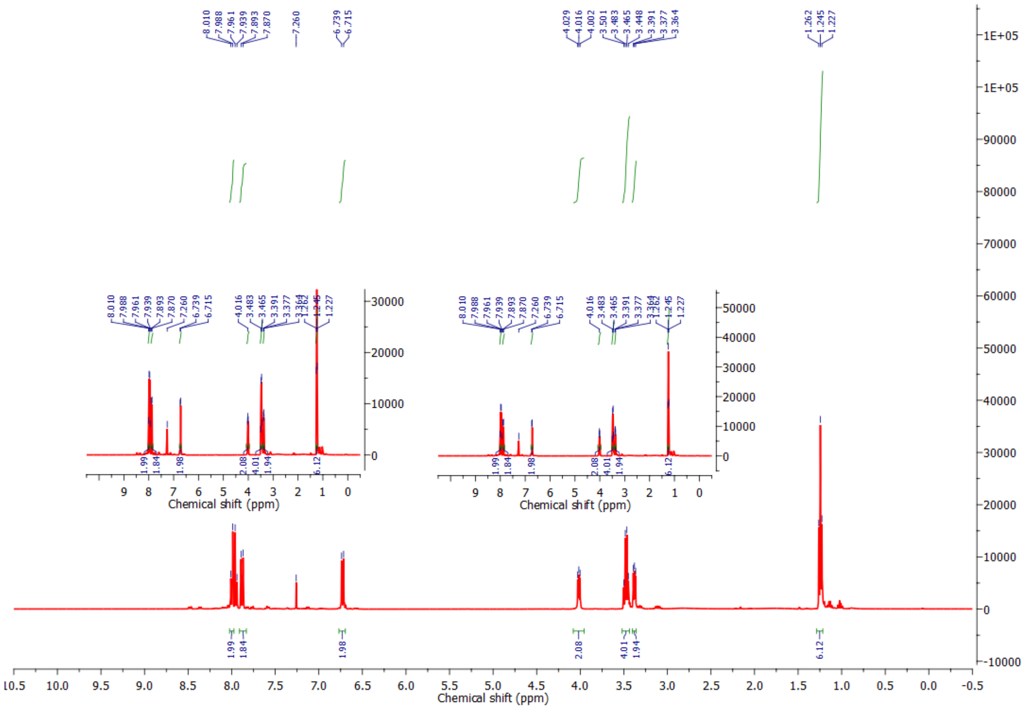


Figure 7.32 ^{1}H NMR spectrum of N, N-diethyl-4-[((4-sulphonylethanol)phenyl)azo]aniline

Figure 7.33 ^{13}C NMR spectrum of N, N-diethyl-4-[((4-sulphonylethanol)phenyl)azo]aniline

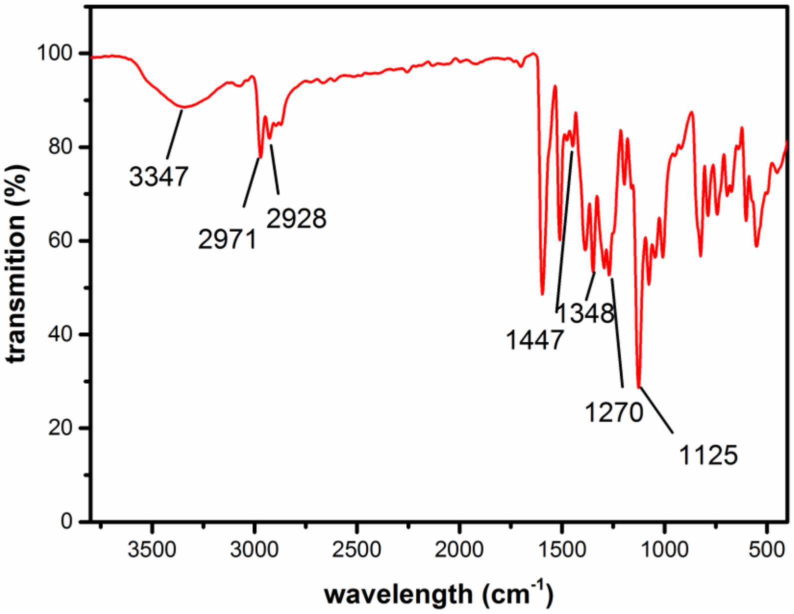


Figure 7.34 FTIR spectrum of N, N-diethyl-4-[((4-sulphonylethanol)phenyl)azo]aniline

7.5.4 Characterisation of N, N-diethyl-4-[(E)-(4-vinylsulfone)phenyl) azo]aniline, RD 5

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 7.35): δ 7.986-7.956 (d, *J* = 9, 2H), 7.938-7.908 (d, *J* = 9, 2H), 7.89-7.86 (d, *J* = 9, 2H), 7.894-7.863 (d, *J* = 9.3, 2H), 6.746-6.715 (d, *J* = 9.3, 2H), 6.737-6.649 (dd, *J* = 9.9 and 9.9, 1H), 6.497-6.442 (d, *J* = 16.5, 1H), 6.057-6.025 (d, *J* = 9.6, 1H), 3.515-3.444 (q, *J* = 21.3, 4H), 1.273-1.226 (t, *J* = 14.1, 6H); C NMR (75 MHz, $CDCl_3$) (Figure 7.36): δ 156.6, 151.2, 143.3, 138.7, 138.6, 129.1, 127.7, 126.3, 122.8, 111.2, 45.0, 12.8; ν_{max}/cm^{-1} (ATR) (Figure 7.37): 3095, 2971, 2900, 1445, 1350, 1268, 1125; m/z (ESI): found 344.1427(M+1); $C_{18}H_{21}N_3O_2S$ requires 344.1433. The UV/Vis spectrum in Figure 7.38 indicated that the dye exhibits a maximum absorption at 461 nm.

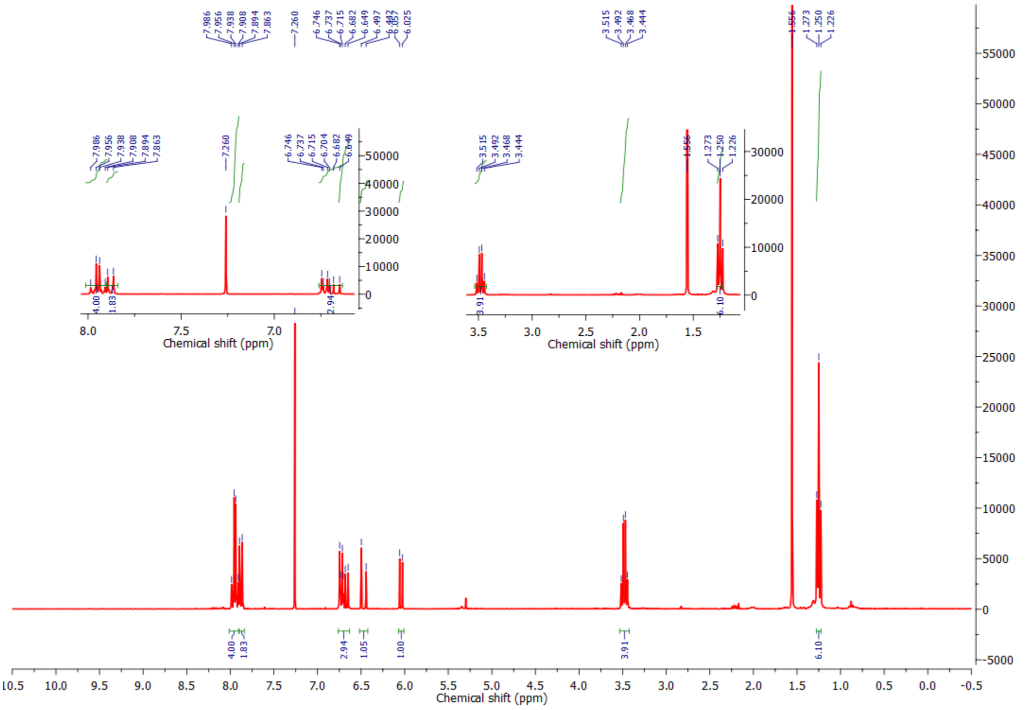


Figure 7.35 ^{1}H NMR spectrum of the RD 5

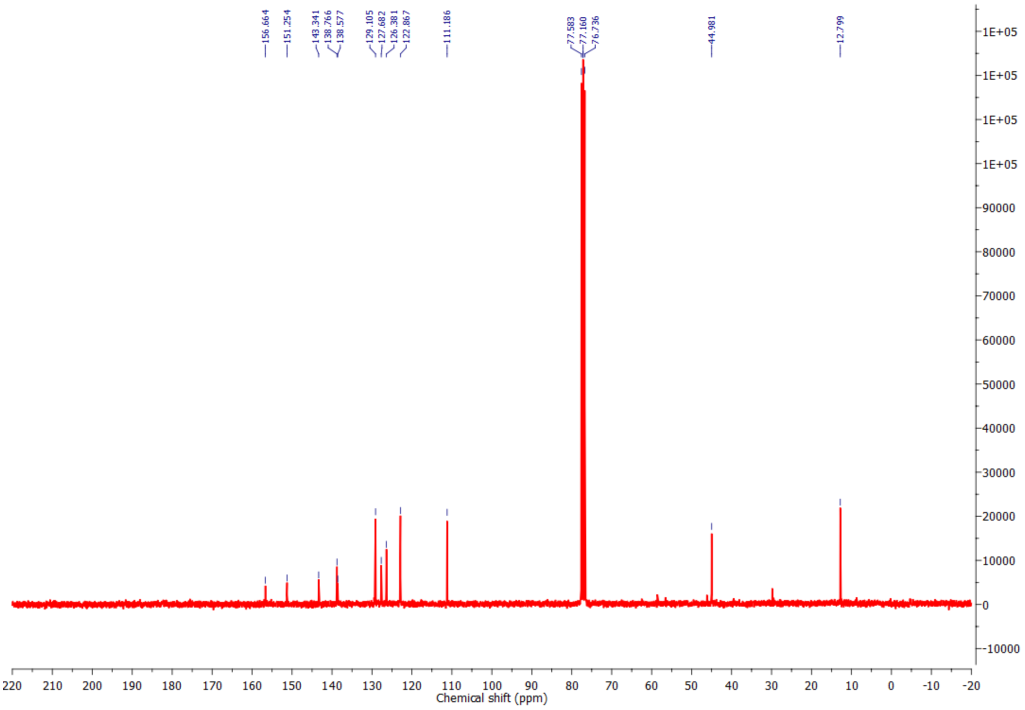


Figure 7.36 ^{13}C NMR spectrum of the RD 5

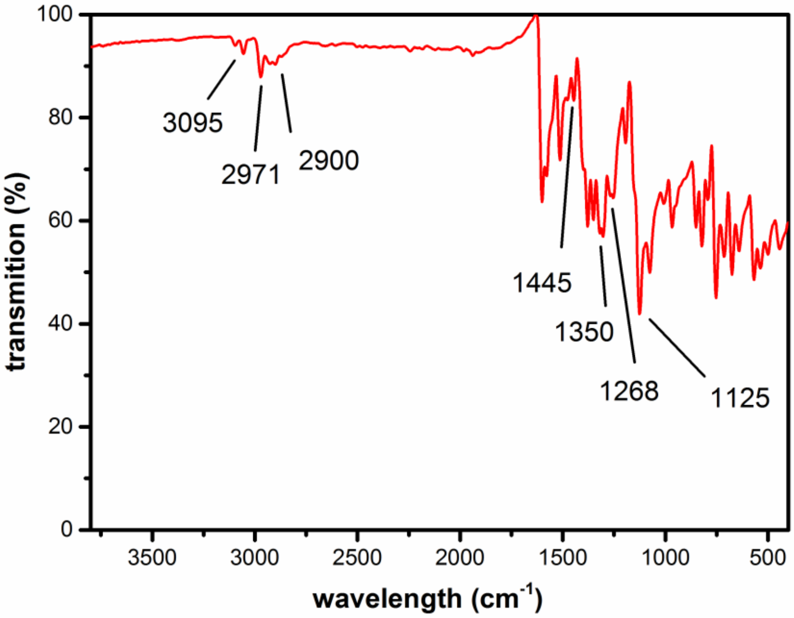


Figure 7.37 FTIR spectrum of the RD 5

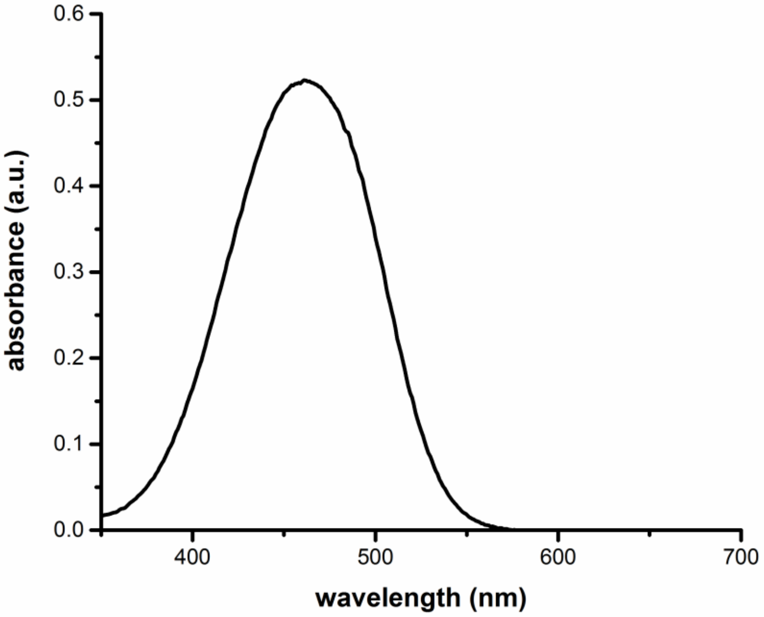


Figure 7.38 UV-vis spectrum of the RD 5

Chapter 8 Conclusions and future work

8.1 Conclusions

Whilst the supercritical technique has been utilised in the dyeing of synthetic textiles successfully to a large extent, the success and the understanding of supercritical dyeing for natural fabrics are still limited. This thesis focused on the synthesis of a variety of reactive disperse dyes and their dyeing application for natural fabrics in $scCO_2$. In summary, five types of reactive disperse dyes were synthesised successfully.

RD 1

RD 1 containing the isocyanate reactive group was synthesised and characterised. RD 1 was based on the commercial C.I. Disperse Orange 3. Compared to other published research, the supercritical dyeing conditions used for $scCO_2$ dyeing with RD 1 were milder [1-3]. A small amount of water was used to pre-treat the fabrics. It was understood that the water remaining on the fabrics after the pre-treatment acted as a co-solvent in the supercritical dyeing. It was seen that the addition of the water in the pre-treatment and dyeing processes helped enhance the qualities significantly for the supercritical dyeing of wool. Thus, the results show that intense colour, excellent fixation and wash fastness were achieved on the dyed wool using RD 1 in $scCO_2$ dyeing. Good colouration was achieved when the cotton fabric was dyed in $scCO_2/H_2O$. However, the fixation of the cotton fabric using RD 1 needed to be improved.

RD 2, RD 3 and RD 4

RD 2, RD 3 and RD 4 were synthesised successfully using ethyl, isopropyl and tert-butyl solubilising groups respectively, in order to increase the solubility of the dyes in $scCO_2$. Wool fabrics dyed with each of these dyes were tested, all giving excellent results in terms of colour strength, fixation and wash fastness (fading and staining). The addition of the solubilising groups to the dye molecules proved to improve the dyeing results for the wool fabrics. The required dyeing conditions to achieve the best dyeing results for wool fabrics in $scCO_2$ were relatively mild. The addition of solubilising groups in the reactive disperse dyes had little effect on the supercritical dyeing for cotton fabric when the isocyanate group was used as the reactive group.

RD 5

The objective of synthesising a reactive disperse dye containing the vinyl sulphonyl group was achieved, with the RD 5 being successfully synthesised. The designed route required no more than four synthetic steps, and it has been shown that purification was not required at any point in the synthesis. The initial precursors used were relatively cheap and the RD 5 appeared to have good solubility in $scCO_2$ under the dyeing conditions employed in this study. Moreover, the route of synthesis of this reactive disperse dye that contain vinyl sulphonyl group can potentially be adapted to dyes of the same class carrying other chromophore groups.

The dyeing experiments involving RD 5 confirmed that the vinyl sulfonyl group is indeed a promising reactive group for the dyeing of both wool and cotton fabrics in $scCO_2$. Wool dyed with RD 5 in $scCO_2/H_2O$ produced excellent fixation, colour strength and wash fastness results. The rate of fixation of RD 5 on the dyed cotton was significantly greater than those of RD 1, RD 2, RD 3 and RD 4. The dyeing conditions employed for dyeing using RD 5 were much milder than the dyeing conditions seen in previous attempts at dyeing natural fibres with other reactive disperse dyes [1-4]. It was identified that a small amount of water in the supercritical dyeing process played a vital role in achieving the best dyeing results for both wool and cotton.

RD 1, RD 2, RD 3, RD 4 and RD 5

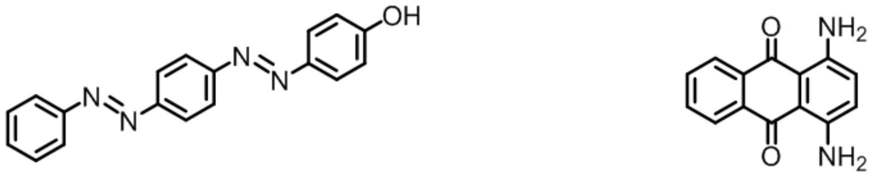
The cross-section analyses of dyed fibres showed that good dye uptake was obtained when a small amount of water was used in the dyeing process using the synthesised dyes at the stated conditions. Little damage on the dyed cotton was observed when the dyes containing isocyanate group were used in the dyeing process.

Overall, significant improvements were achieved when the reactive disperse dye containing either the isocyanate group or vinyl sulphonyl group was used in the supercritical dyeing process. The introduction of solubilising groups on the synthesised reactive disperse dyes helped to improve the dyeing ability of the dye in supercritical dyeing. Water had been shown to play a significant role in the pre-treatment process and dyeing process.

8.2 Future work

Even though successful supercritical dyeing of wool has been achieved, the dyeing of cotton is still unsatisfactory. To achieve a better dyeing for cotton in $scCO_2$, and to obtain different range of colours of dyes for $scCO_2$ dyeing, researches can be carried out in the following areas.

Further research may focus on the syntheses of reactive disperse dyes of different dye chromophore structures (examples of different chromophore group are shown in Figure 8.1) covering a large range of colours via modification with a range of solubilising groups, such as alkyl chains of different lengths. The chromophore structures that give strong colours can then be modified with either isocyanate groups or vinyl sulphonyl groups to increase the reactivity towards natural fabrics in $scCO_2$ dyeing. General structure of a novel reactive disperse dye is depicted in Figure 8.2.



example of azo dye

example of anthroquinone dye

Figure 8.1 Examples of chromophore groups that can be used to synthesis novel reactive disperse dye for the $scCO_2$ dyeing

Furthermore, it will be important to test the dye solubility in $scCO_2$ to fully understand the effects of the different dye structures on the efficiency of the dyeing process.

A full understanding of the mechanism of the dyeing may be explored. Moreover, evidence of the formation of covalent bonds between the dye molecules and the dyed fabrics need to be analytically verified.

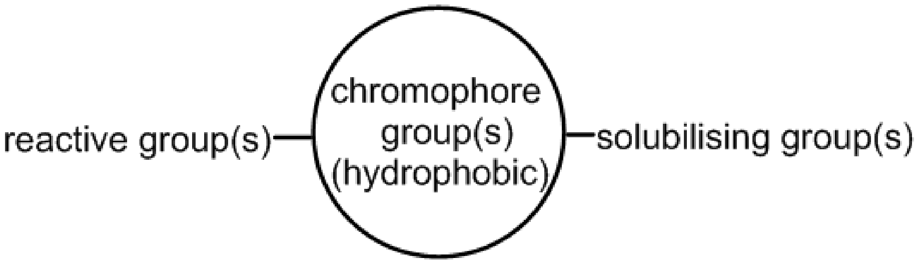


Figure 8.2 General structure of a novel reactive disperse dye

Finally, in order to obtain the most desirable dyeing results, not only thorough chemical investigations but also mechanical investigations need to be conducted. Well-designed facilities of $scCO_2$ dyeing are very important. Good circulation of the CO_2, ideal rotation of the beam etc. would have positive impacts on the dyeing results. Only the combination of the technologies chemically and mechanically can allow the technology to reach its potential in the commercially viable industrialisation of the supercritical dyeing for natural fabrics.

8.3 References

1. Zhang, Y.-Q., Wei X.-C., and Long J.-J., *Ecofriendly synthesis and application of special disperse reactive dyes in waterless coloration of wool with supercritical carbon dioxide.* Journal of Cleaner Production, 2016. **133**: p. 746-756.
2. Van der Kraan, M., F. Cid, G. Woerlee, W. Veugelers, and G. Witkamp, *Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes.* The Journal of Supercritical Fluids, 2007. **40**(3): p. 470-476.
3. Zheng, H., Y. Xu, J. Zhang, X. Xiong, J. Yan, and L. Zheng, *An ecofriendly dyeing of wool with supercritical carbon dioxide fluid.* Journal of Cleaner Production, 2017. **143**: p. 269-277.
4. Banchero, M., *Supercritical fluid dyeing of synthetic and natural textiles - a review.* Coloration Technology, 2013. **129**(1): p. 2-17.