Clean production using supercritical processing: an example of dyeing Tencel® and Nylon66 fabrics with recycling hydrophobic reactive dyes

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Abstract

In current industrial textile dyeing processes, large amounts of wastewater are produced. This is an environmental burden and, due to the ever more stringent regulations on water pollution, also an economical problem. Only industrial waste minimization can give consideration to environment-friendly concerns. Now we have the notion of Reduce, Reuse and Recycle for environmental protection and economic development. The use of supercritical fluid processes such as the dyeing method solves this problem: the residual dye remaining in the dye bath after the process can easily be separated and can be recycled. The supercritical dyeing method has several benefits, such as being nonflammable, nontoxic, easy to use, economic and with favorable waste treatment processes.

In order to achieve Green Production, this paper explores the feasibility of using Cationic surfactant KC-3A (Quaternary ammonium salt), recycling C.I. Reactive Blue 4 (DCT type) and C.I. Reactive Blue 19 (VS type) dyes to the original dyeing process and further dyeing Tencel® and Nylon66 fabrics with supercritical fluid. The recycled dye's structure is determined by spectroscopy. This paper also discusses both recycling dyes, dyeing Tencel® and Nylon66 fabrics in exhaustive dyeing processes. The experimental results showed that Tencel® fabrics after pre-treatment were dyed by the supercritical dyeing method with good fastness properties and acceptable color depth, and dyeing Nylon66 fabrics with recycling dyes is satisfactory using the supercritical dyeing method.

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Finally, this paper also shows that dyed Tencel® achieved optimum dyeing results at 140°C and 300 bar and dyed Nylon66 obtained optimum dyeing results at 120°C and 300 bar. The fixations on Nylon66 and Tencel® being above 77%, are also dependent on pressure and temperature. The washing and rubbing fastness of all dyed fiber is rated at between 3–4 and 5.
Keywords: recycling, supercritical fluid, reactive dyes, cationic surfactant, hydrophobic.

1 Introduction

In the 21st century, as a result of photochemistry development, humanity may be able to obtain synthetic fiber to replace all natural fibre including, cotton, flax, wool and silk. Although natural fiber has many uses, including supplying the family with clothing and fabric, the use of synthetic fiber has overtaken natural fibers due both to mass production and cost reduction improving product diversification all over the world. Tencel® fiber is made using environment-friendly techniques. Tencel® fiber has the common cellulose fiber characteristics: good intensity, good moisture absorption permeability, strong anti-static properties, good draping, a soft feel, comfortableness, and the tangibility is fine. It also has characteristics which cellulose does not: the shrinkage is low, size stability good, has silk gloss, and its textile fiber officially established moisture content is 6.3%. Due to its fine functionality and the environment-protection, it is honored as the 21st century's green environmental protection textile fiber.

Supercritical fluid is defined as fluid processed beyond the critical point where it is indistinguishable as a liquid or a gas [1–3]. Gases and liquids could become supercritical fluids when they are compressed and heated above their critical pressure and temperature. In this state it can demonstrate properties intermediate between those of typical gases and liquids. The supercritical carbon dioxide dyeing method has several benefits, such as being nonflammable, nontoxic, easy to use, economic and environmentally acceptable. The technique became more attractive since Saus *et al*. [2] studied the dyeing of polyester and modified natural fibers with disperse dyes in supercritical carbon dioxide [4–7]. In their context, the authors reported that temperature and pressure were the main factors which could affect dyeing performance. It has been demonstrated that supercritical carbon dioxide is a good medium for polymer dyeing, but some factors which affect the results such as pressure, temperature, dye concentration, pH value and the addition of assistant agents still need to be understood. We used supercritical fluid dyeing technology to dye Nylon66 and Tencel® with a 180ml capacity dye pot, raising the pressure and temperature simultaneously [8].

2 Experiments

2.1 Hydrophobic dyestuff preparation

In this research, first C.I. Reactive Blue 4 (dichlorotriazine type) and C.I. Reactive Blue 19 (vinylsulphone type) dyes would be used to dye Tencel® fabric in the dyeing bath, with separately adjusted pH values, for 60 minute of dyeing time. Then we removed the dyeing residue to carry out the recycling dye procedure and calculated the recycling dye ratio. For this research, the recycling dye procedure uses a dye liquor of titrate ammonium salts (KC-3A), which is a surface active agent, the temperature is slowly elevated to approximately 80ºC until an obvious aerosol is obtained, or a stop in heating agitation, when the precipitation separation is presented. It causes its precipitation using the centrifuge to be obvious. Connection the lower precipitation intermixture neutral pH value to 7, after neutral, the centrifugal separation is repeated. The precipitation will then put in a flask with acetone and then the solvent removed to obtain the final product, which namely will be used as the recycling dye for this research institute. In order to confirm the dye structure in the recovery procedure, electronic spectra data of the dyes are shown. The structure of dye was determined by FTIR, ^{1}H NMR, EA and MS analysis. IR spectra of dyes were obtained on Shimadzu FTIR-8300 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM 400 machine using [$^2H_6$]DMSO as a solvent and the MS datum were obtained on a Joel HX110 mass spectrometer. EA analysis was carried out on a Heraeus CHN[O] Rapid F002 apparatus. The results obtained show dye recovery ratio above 60 %, as shown in Table 1. The reaction between the fiber and dye is represented in scheme 1. [9] Indeed, the dye-fiber interaction between terminal amine group of Nylon66 and vinylsulphone group of dye was also the covalent bond formed between the hydrophobic reactive dye and Nylon66 fiber.

$$\text{Dye—}SO_2\text{–}CH\text{=}CH_2 + NH_2\text{—Nylon—COOH} \longrightarrow$$

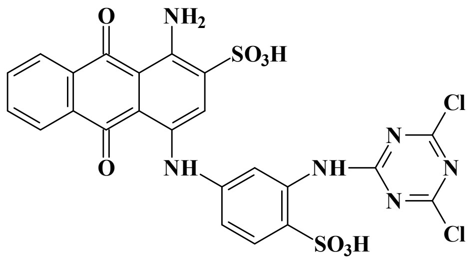
$$\text{Dye—}SO_2\text{–}CH_2CH_2\text{–NH—Nylon—COOH}$$

Table 1: Recovery ratio of recycling dye procedure with KC-3A.

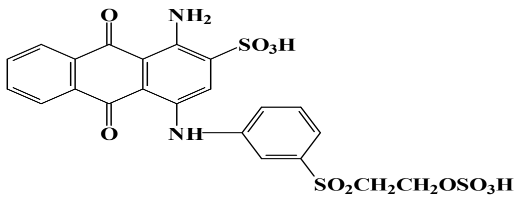
Dyes	Recovery ratio	Appearance of precipitate
C.I. Reactive Blue 4	63.2 %	Blue(RB 4)
C.I. Reactive Blue 19	61.6 %	Deep blue(RB 19)

Scheme 1

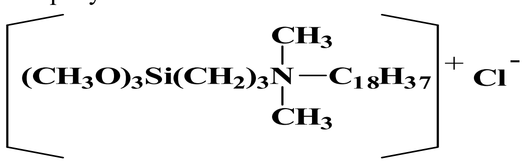
P.S. (1) C.I. Reactive Blue 4 (molecular weight：637.43) supply from Chung Fu Dyestuff Company.



(2) C.I. Reactive Blue 19 (molecular weight：626.54) supply from Telu International Trade Company.



(3) Ammonium salts (KC-3A) (molecular weight：495.88) supply from Chung Fu Dyestuff Company.



2.2 Material and apparatus

A commercial desizing, scouring, unfinished fabrics of plain cloth was employed in the form of 12 cm x 4 cm samples. The Tencel® fabrics (warp density 120 pick/inch and weft 76 pick/inch, width 30”) and Nylon66 fabric

$$\frac{109\times 66}{(\,70d/66f\times 156d/132f\,)}$$

were purchased from Formosa company. The apparatus used for the dyeing procedure was manufactured by the Zaar technical company. Figure 1 is a diagram of supercritical carbon dioxide dyeing system. It can be pressurised and heated up to 400 bar and 200ºC, respectively. When optimum pressure is reached, carbon dioxide is released and the flow rate maintained at 150 ml/min by adjusting valve until the pressure is down to atmosphere. The tube was covered with heating line to avoid the drastic precipitation of dye.

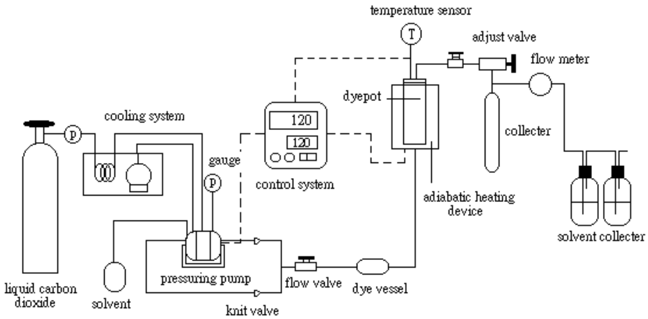


Figure 1: Diagram of supercritical carbon dioxide dyeing system.

2.3 Dyeing procedure and fastness testing

Approximately 1 g of fabric and an appropriate amount of dye (4 % o.m.f.) were put into the dye pot and dye vessel, respectively. The fabric was wound into the dye pot, the apparatus was sealed and then heated to the dyeing temperature (100°C, 120°C and 140°C) while carbon dioxide was pumped to the pressure 300bar. In the dyeing procedure, we raised pressure and temperature at the same time at a 4°C /min rate. Each dyeing was maintained for 10 minutes and then the pressure step released. At each step, 20 bar of pressure was reduced and temperature still kept at the dyeing temperature for 30 seconds until the pressure was down to 75bar and then down to atmosphere directly. The dye uptake, determined as already reported by reflectance analysis according to the Kubleka-Munk equation, was expressed in terms of the K/S value. We measured dyed materials to get the reflectance (R), and calculated the apparent color yield using a color matching system. With the formula described below

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

Color fastness to artificial light was determined using a Xenon arc light fastness tester, according to ISO 105 B01 method (1978). Furthermore, dyed fabrics were immersed in a boiling pyridine-water (25:75) solution to extract any unfixed dye. On treated and untreated specimens, the determination of washing fastness was carried out according to the ISO 105 $C0_2$ method (1989).

3 Results and discussion

3.1 Spectrum analysis

First, Figure 2 shows that the structure of KC-3A was checked by full spectrum analysis. The band at 3200-3550 cm^{-1} for KC-3A in FTIR spectrum was corresponding to the -OH stretch band. The band located within the 1636 cm^{-1} peak indicated the H-O-H bend vibration absorbance. Another band located within 1455 cm^{-1} and 1380 cm^{-1} indicated the C-N stretch band on ammonium salts. Absorption at 2925 cm^{-1} of KC-3A was C-H stretch band of the CH_2 and CH_3 group. Second, the structure of hydrophobic reactive dye, including C.I. Reactive Blue 4(RB 4), C.I. Reactive Blue 19(RB 19), Recycled Reactive Blue 4 (RRB 4, hydrophobic dye), and Recycled Reactive Blue 19 (RRB 19, hydrophobic dye), was checked by full spectrum analysis. The band at 1600-1605 cm^{-1} for these dyes in FTIR spectrum corresponds to the C=C stretch band. Another band located within 1520-1580 cm^{-1} range indicated the triazine band of RB 4 and RRB 4. Comparing both RB 4 and RRB 4, absorption at 2915 cm^{-1} and 2940 cm^{-1} were $-CH_2-$ stretch band by hydrophobic dyestuff. It is clear that hydrophobic dyestuff was synthesized by KC-3A and RB 4. In other words, both Figures 3 and 4 demonstrate the successful synthesis of these hydrophobic reactive dyes.

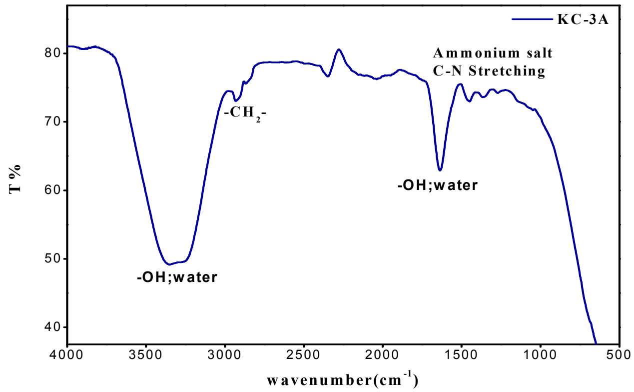


Figure 2: The FTIR spectrum of KC-3A.

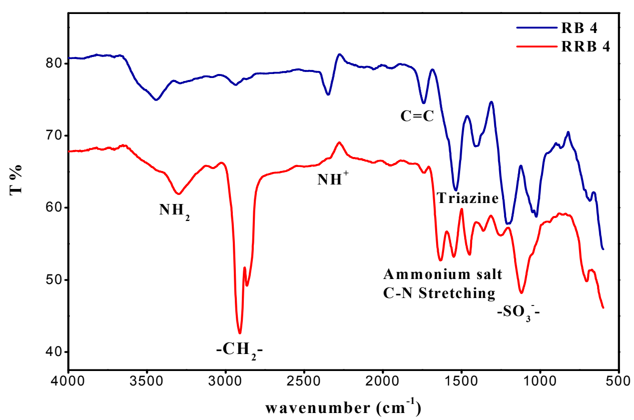


Figure 3: The FTIR spectrum of C.I. Reactive Blue 4(RB 4) and Recycled Reactive Blue 4 (RRB 4, hydrophobic dye).

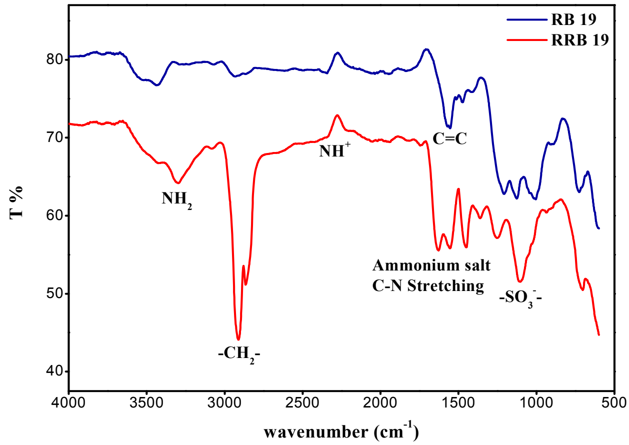


Figure 4: The FTIR spectrum of C.I. Reactive Blue 19(RB 19) and Recycled Reactive Blue 19 (RRB 19, hydrophobic dye).

3.2 Color strength

At pressures below 200 bar, dyestuff dissolved in the fluid is low. When pressure reaches 250 bar to 300 bar, the dyestuff dissolves at the best conditions set by this experiment, because lower pressure means better economic efficiency and safety, but dyeing quality must be taken into account. The low viscosity and high density of supercritical fluids makes the dyestuff penetrate easily into the Tencel® and Nylon66 fibers. When Tencel® and Nylon66 were dyed with RRB 4 and RRB 19 at 200 bar to 300bar with 4 % (o.m.f.) of dye concentration for 10 min, the dyestuff attached not only to the outside of the yarn bundle but penetrates to the inside of the yarn. As the dyeing procedure was completed, the fabric was then immersed in a boiling pyridine-water (25:75) solution to extract any unfixed dye and dried at 80°C for 30min. Tables 2 and 3 show the color strength (K/S) with hydrophobic reactive dyes on Tencel® and Nylon 66 fabrics.

At dyeing temperature (140°C), these phenomena become more serious on Nylon66 fibers because of thermal properties. Dyeing results with hydrophobic dyes indicated that dye absorbance increases with an increase in pressure. Comparing results from the trials of two dyestuffs, RRB 19 showed better penetration efficiency. As compared with water dyeing specimens, whose K/S values are 1.15 and 1.20 for RRB 4 and RRB 19 at 100°C, dyeing with supercritical fluid will have higher exhaustion for RRB 4 and RRB 19 at 300 bar pressure. In the experiment, we can conclude that both temperature and pressure affect the penetration and hydrophobic dyestuff selection is an important factor for achieving optimum dyeing results. In other words, it is practicable that the recycling reactive dye is used by supercritical processing in dyeing technology.

Table 2: K/S value of RRB 4 and RRB 19 dyeing Tencel® fabrics.

Temperature	Hydrophobic dye	Pressure(bar)		
		200	250	300
100 ℃	RRB 4	1.02	1.65	2.87
	RRB 19	2.98	3.16	3.90
120 ℃	RRB 4	1.85	2.43	3.76
	RRB 19	3.78	5.08	6.92
140 ℃	RRB 4	2.62	3.65	4.41
	RRB 19	4.12	5.65	7.60

Table 3: K/S value of RRB 4 and RRB 19 dyeing Nylon66 fabrics.

Temperature	Hydrophobic dye	Pressure(bar)		
		200	250	300
100 ℃	RRB 4	3.18	4.05	4.42
	RRB 19	5.02	6.13	6.20
120 ℃	RRB 4	4.68	6.26	6.28
	RRB 19	6.45	7.78	8.68
140 ℃	RRB 4	4.12	5.72	5.68
	RRB 19	5.21	7.12	8.25

3.3 Fastness

Data on color fastness to washing was shown in Table 4. Comparing the washing fastness at a temperature of 120°C and dye concentration of 4% (o.m.f.) in the supercritical dyeing system, results showed that the specimen of Tencel® and Nylon66 fabrics have fade gray color specification of about 3–4 grades. It was confirmed that the color yield of the Tencel® and Nylon66 fabrics treated under supercritical fluid dyeing processes was competitive with that of the commercially available in the market, which is satisfactory for normal application. The rubbing fastness results showed almost 4-5 grades, as shown in Table 4, which was likely to be similar to that achieved with monumentalized acid dyes. Besides, hydrophobic reactive dyes for Nylon66 offer real potential for producing dyeing of higher washing fastness compared to those produced from acid or disperse dyes. Above all, the results found that it has not been possible to dye these fibers in this medium with good fastness properties and to acceptable color depth. The positive effect of long alkyl of quaternary ammonium salt recycling dyes is due to the effect of increased molecular weight and due to an effect of reactive groups on the reactivity of the dye–fiber system to diminish where the alkyl chain increases the hydrophobicity of the dyestuff.

Table 4: Fastness of Tencel® and Nylon66 fabrics dyed with hydrophobic reactive dye.

Dyed fabrics	Dye code	Pressure	Washing fastness (staining on Nylon66)		Rubbing fastness (staining on cotton)
			before extraction	*after extraction	*after extraction
Tencel®	RRB 4	200 bar	4 (5)	5(5)	4-5 (5)
		250 bar	4 (5)	5(5)	4-5(4-5)
		300 bar	4 (5)	5(5)	4-5(4-5)
	RRB 19	200 bar	4 (5)	5(5)	5(5)
		250 bar	4 (5)	5(5)	4-5(4-5)
		300 bar	3-4(5)	5(5)	5(5)
Nylon66	RRB 4	200 bar	3-4(5)	5(5)	5(5)
		250 bar	4(5)	5(5)	5(5)
		300 bar	3-4(5)	5(5)	5(5)
	RRB 19	200 bar	4(5)	5(5)	5(5)
		250 bar	4(5)	5(5)	4-5 (5)
		300 bar	3-4(5)	5(5)	5(5)

4 Conclusions

Using supercritical carbon dioxide as a dyeing medium for Tencel® and Nylon66 fabrics can eliminate the pollution of water treatment and save time. Cost of investment can be balanced by pollution and processing profits. The dyeing of Tencel® and Nylon66 fabrics with hydrophobic reactive dyes synthesized in our laboratory was quite feasible. The work indicated that both temperature and pressure are the factors which affect the color strength of Tencel® and Nylon66 with hydrophobic reactive dye using supercritical carbon dioxide as solvent system. Rubbing fastness was satisfactory for normal applications and washing fastness was excellent as hydrophobic reactive dyes were used to dye Tencel®

and Nylon66 fabrics. In accordance with the results stated above, we can deduce that the potential benefit of supercritical carbon dioxide as solvent system is widely proved. This experiment demonstrated the possibility of dyeing polar fabric with supercritical fluid dyeing method. Supercritical fluid dyeing process is an effective replacement for traditional water process dyeing for synthetic polymers. Thus the development of this technology is available and great progress may be expected for another polymer fiber in future.

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