ABSTRACT

FEI, XIUZHU. Decolorization of Dyed Polyester Fabrics using Sodium Formaldehyde Sulfoxylate. (Under the direction of Dr. David Hinks and Dr. Harold S. Freeman).

Polyethylene terephthalate (PET) fiber is now the largest single fiber type within global textile production, taking over from cotton. In view of environmental stewardship, an effective approach to recycling colored PET fabrics has drawn wide attention. A key step in the recycling process is dye removal. Disperse dyes are used to dye PET fibers and designed to be durable inside the fiber. In addition, disperse dyes are hydrophobic and will not be substantially extracted with water as the only solvent. In this work, the organic solvent, acetone, was used in combination with water to remove disperse dyes from the PET, and sodium formaldehyde sulfoxylate (SFS) was employed to decolorize the dye. This agent was found effective for decolorizing Disperse Yellow 42, Yellow 86, Blue 56 and Blue 60 in acetone/water solutions and the process was extended to decolorization of dyed PET. An optimized combination of treatment time (30 min), water to acetone ratio (1:2), SFS concentration (10g/L), temperature (100 °C), and liquor ratio (1:50) was found to give sufficient color removal for a broad range of disperse dyes. Reuse of the water/acetone medium for five times was achieved for decolorization of Disperse Yellow 42 but could not be achieved for Disperse Blue 56. Fabric strength assessments were also investigated. It was found that SFS decolorization has no adverse influence on PET strength, as judged by viscosity measurements.
Decolorization of Dyed Polyester Fabrics using Sodium Formaldehyde Sulfoxylate

by

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DEDICATION

I dedicate my thesis work to my parents and sister. A special feeling of gratitude to my loving parents, Mengqiao Fei and Yuchai Zhang who give me endless support and encouragement.

My sister Xiudong Fei has never left my side and is very special.
BIOGRAPHY

Xiuzhu Fei was born on November 30th, 1991 in Shaoxing, Zhejiang Province of China. She is the second daughter of Mengqiao Fei and Yuchai Zhang. She was graduated from Ronghuai Private School in June, 2009, and became a student in Jiangnan University majoring Dyeing and Finishing Engineering. After she obtained her bachelor degree in 2013, she was enrolled in North Carolina State University to pursue her Masters degree in Textile Chemistry in the College of Textiles.
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CHAPTER 1 Introduction

1.1 Thesis Outline

This thesis contains seven chapters. Chapter 1 is a general introduction which outlines the major parts and research objectives of the thesis. Chapter 2 is the literature review of polyethylene terephthalate (PET), dyes for PET, decolorization methods for dyes in aqueous solutions and the properties of a strong reducing agent, sodium formaldehyde sulfoxylate. Chapter 3 is the experimental section, describing the materials, equipment used in the research. It presents the preliminary experiments including standard dyeing procedure and decolorization of solution and commercial polyester fabrics. Meanwhile it provides detailed information about statistical DOE, control experiments and characterization methods of decolorization performance. Chapter 4 presents the results and discussion regarding some preliminary experimental results, and results of optimization steps. Intrinsic viscosity and viscosity-average molecular weight of treated PET fabrics have also been discussed. Chapter 5 summarizes the conclusions achieved in research done to date. Chapter 6 gives a short discussion on recommended future work. Chapter 7 is a list of references cited throughout the thesis.

1.2 Research Objective

This thesis research has following objectives:

(1) To develop a novel approach to decolorizing polyethylene terephthalate fabrics using sodium formaldehyde sulfoxylate (SFS) as reducing agent in an aqueous system, and produce well prepared white polyesters with minimal fiber degradation.
(2) To optimize a SFS decolorization process with high efficiency and low chemical, energy, time and water consumption via a statistic central design of experiments and control experiments, to achieve the optimized treatment time, SFS concentration, ratio of water to acetone, temperature and liquor ratio with K/S values and CIE Whiteness Index as the output.

(3) To apply the optimized process to normal polyester dyed by various disperse dyes as well as to cationic dyeable polyester dyed by basic dyes.
Chapter 2 Literature Review

2.1 Nature of Polyethylene Terephthalate

Polyester is a category of polymers that are characterized by the presence of ester functional groups in their main chain. Polyesters include natural chemicals, such as cutin, which is a main component of plant cuticle and consists of omega hydroxyl acids and their derivatives linked via ester bonds [0], as well as synthetic chemicals, such as polyester terephthalate and polylactic acid. Natural polyesters and a few synthetic ones are biodegradable, but most synthetic polyesters are not. Polyester can be classified as thermoplastic and thermoset, according to their chemical structures. There are also polyester resins cured by hardeners. The most common polyesters are thermoplastics [2]. Although polyester is board range of various polymers, the term “polyester” as a specific material in textile, usually refers to polyethylene terephthalate. Polyethylene terephthalate, commonly abbreviated PET, PETE, is a thermoplastic polymer and the most common type among the polyester family. Apart from its application in textile, PET has been made into durable crystal-clear beverage bottles and other liquid containers by improved stretch-molding procedures. PET bottle is commonly recycled, and has the number 1 as its recycling symbol.

2.1.1 The History of PET

The history of thermoplastic polyester goes back to the beginning of twentieth century with the pioneering work of Carothers. At the turn of the nineteenth century, there were natural fibers, cotton, wool, silk, and rayon dominating the market. During 1920s, Herman Staudinger, a great German chemist demonstrated the existence of macromolecules, which he
characterized as polymers. In 1926, Charles Stine, the vice-president of DuPont who created the laboratory from which nylon and other significant inventions were made, proposed to the DuPont Company that they should invest in this unproven concept of polymers. After more than 10 years of extensive research effort by Carothers and his team, DuPont Company announced a big news to the world that they had developed a textile fiber, nylon 66. PET, the first aromatic polyester of importance was prepared and patented with the name Terylene by John Whinfield, James Dickson and their employer the Calico Printers’ Association of Manchester in England in 1947. In 1953, PET was produced commercially as fiber for textile industry with a new name Dacron by DuPont using modified nylon technology. DuPont polyester research rapidly leads to a whole range of trademarked products as Mylar, Nomex and Kevlar during 1960s and 1970s.

2.1.2 The Preparation of PET
In laboratory scale, PET can be synthesized by the polymerization of terephthalic acid and ethylene glycol with the byproduct of water. Ethylene glycol is a colorless liquid obtained from ethylene, and terephthalic acid is a crystalline solid obtained from xylene. Esterification of these two compounds is conducted directly at moderate pressure (2.7–5.5 bar) and high temperature (220–260 °C). Water should be eliminated in the reaction, and it is continuously removed by distillation. Therefore PET is produced in the form of a molten and viscous mass. Large-scale production of PET proceeds via a two-step process. Dimethyl terephthalate (DMT) and excess ethylene glycol are reacted with the aid of one or several catalysts, to form di-(2-hydroxyethyl) terephthalate at temperature ranging from 150 to 200 °C. Methanol is removed
by distillation in order to drive the reaction forward. Subsequently, the product obtained from this transesterification is polycondensed under high vacuum at 270-280 °C, with continuous distillation of ethylene glycol as well.

The reactions are idealized as follows and shown in Figure 1 and 2:

1. First step: transesterification

![Figure 1 Tranesterification reaction.](image)

2. Second step: polycondensation

![Figure 2 Polycondensation reaction.](image)

This manufacturing process is based on the original patent of Whinfield and Dickson [3].

2.1.3 The Characteristics of Polyethylene Terephthalate Fibers

Although many new synthetic fibers have been development within the last decades, it cannot be claimed that polyester has been replaced by other fibers in the textile market. Polyester fibers still occupy a leading position among all commercial fibers—world production is greater
than the production of all the other fibers. The properties of polyester fibers have been studied most completely. Due to its specific physical and chemical properties, polyester is predestined for a quite definite purpose so that it cannot be easily substituted [4].

2.1.3.1 Physical Properties

2.1.3.1.1 Appearance

Polyester fibers have a faintly tint of ivory, and have a smooth longitudinal appearance. Generally, polyester fibers are produced with a round cross-section. However, profiled cross-sections, such as star-shaped, H-shaped, and hollow cross-sections have also been developed due to their certain advantages [5]. Hollow fibers, for example, as a consequence of the air ducts in the hollow, there is a greater heat retention, and also a lower density.

2.1.3.1.2 Mechanical Properties

The mechanical properties of fibers, no matter whether they are natural or synthetic, mainly determine the quality of the manufactured textiles and can therefore be regarded as the most significant of textile properties.

PET exhibits interesting physical properties. PET, in its purest form, is an amorphous glass-like material. Under the influence of direct modifying additives it develops crystallinity. When heated above its glass transition temperature, PET changes from a rigid glass-like state into a rubbery elastic form where the polymer molecular chains can be stretched and aligned in either one direction to form polyester fibers, or in two directions to form films and bottles [6]. In another words, polyester fiber is obtained in the oriented form. The simplest way to evaluate
the mechanical property of a material is to establish the stress-strain curve or load-elongation curve (Figure 3).

![Stress-Strain Curves for a Material](image)

Figure 3 Stress-Strain Curves for a Material.

From this curve, it is easy to obtain the Young’s modulus (or elastic modulus), the strength at break ($\sigma_r$) and strain at break ($\varepsilon_r$). Tensile strength (or tenacity) also can be calculated by knowing these values. Polyester fibers are commonly characterized by high values of both Young’s modulus (2-2.7GPa) and $\sigma_r$ and low $\varepsilon_r$ value. Normal tenacity polyester fibers, for instance, have the values of $\sigma_r$ around 3400-6350 MPa and $\varepsilon_r$ around 19-40%. For high tenacity polyester fibers, $\sigma_r$ increases up to 7300-11550 MPa with $\varepsilon_r$ values as low as 10-13%. Because of the high elastic modulus, polyester fibers possess very good elastic recovery. This capacity of recovering rapidly imparts polyester fibers with distinguished properties, for example, excellent crease resistance, and very good dimensional stability [7].
While using textile products, abrasion is an undesirable but inevitable effect of exposure to normal use. The abrasion resistance of polyester fibers does not as excellent as polyamide fibers, but approximately equals to or surpasses the values of other synthetic fibers many times, such as polyacrylonitrile, viscose and acetate fibers [7].

2.1.3.1.3 Thermal Properties
The better the thermal properties of a synthetic fiber, the more widespread the application. Thermal properties of PET are greatly affected by the presence of the aromatic phenyl group, which is substituted in para positions and provides an overall stiffness of the polymer repeating unit [5]. It helps to explain the relatively high thermal stability of polyester fibers. The glass transition temperature ($T_g$) is between 67 and 81°C, and the experimental melting point ($T_m$) of commercial polyester fibers is in the range of 255-260°C. Dyeing polyester fibers requires high temperature (130°C), since elevated temperatures can reduce the intermolecular interactions between polymer chains and increase the kinetic energy of the dye molecules. The $T_m$ of synthetic fibers directly influence the subsequent treatment of the textiles produced from these fibers. For instance, textiles made from polyester can withstand contact with an iron which is heated to 170-180 °C without any damages.

2.1.3.1.4 Weather Resistance
The weather resistance of a fabric, which means its ability to hold up against deterioration from exposure to harsh elements, including strong sun, wind, rain, humidity etc., is largely determined by the thermal and water sorption properties. Polyester fibers show very good resistance to weather influences [8]. Products made from polyester can withstand temperature
as low as -40 °C and prolonged exposure to sunlight up to 1000 hours without appreciable loss of strength. Also complete immersion in cold or hot water for many weeks will barely decompose their structure.

In summary, PET in its natural state is nearly colorless. It can be semi-rigid to rigid, according to how it is processed, and it is very lightweight. The presence of a large aromatic ring in the repeating units gives the PET notable stiffness and strength, especially when the polymer chains are aligned with one another in an orderly arrangement. The high-strength textile polyester fiber is made in such semicrystalline form. The stiffness and rigidness of polyester fibers make them highly resistant to deformation. Therefore they impart excellent resistance to wrinkling in fabrics, which makes them popular to produce durable-press blends with rayon, wool and cotton.

2.1.3.2 Chemical Properties

The essential feature which distinguishes polyester fibers from other synthetic fibers is their excellent resistance to a wide range of chemicals [9]. However, in accordance with the chemical structure of PET, the ester linkages should undergo hydrolytic attack by acids and alkalis. In fact, the acid and alkali resistances are much better than expected due to the high crystallinity of polyester fibers.

2.1.3.2.1 Solubility

PET is insoluble in mostly all organic solvents. It is only possible to obtain PET solutions by using o-chlorophenol, trifluoroacetic acid, hexafluoroisopropanol (HFIP) and a mixture of
phenol and trichloroethane [9]. In such solvents, Mark-Houwink-Sakurada relationships [10] can be established:

\[[ \eta ] = K M_v^a \]  \hspace{1cm} (1)

Where \([ \eta ] (\text{mL/g})\) is the intrinsic viscosity, \(M_v\) is the viscosimetric-average molar mass and \(K\) and \(a\) are parameters depending on solvent and temperature. In industry, molar masses are not generally directly obtained. Intrinsic Viscosity (IV) is often measured and related. By using this equation, it is possible to calculate the average \(M_v\) when knowing the intrinsic viscosity [11].

2.1.3.2.2 Resistance to Water

When discussing the mechanical property with regard to weather resistance of products made from polyester fibers, it was stated that longtime immersion in water hardly diminishes their strength. However, boiling water or steam will cause significant hydrolytic degradation of polyester fibers. The hydrolytic degradation induces chain scission and yields to the formation of carboxylic acid and alcohol. It is an important problem associated with many commercial applications.

2.1.3.2.3 Resistance to Acids

On the whole, polyester fibers or filaments show a very good resistance to the dilute corrosive acids \(H_2SO_4\), \(HCl\), \(HNO_3\) and \(H_3PO_4\). But the resistance extent depends on other factors, such as temperature, concentration and duration of treatment. Test disclosed that, treatment with 30\% \(H_2SO_4\) at 80 °C for 5 days did not reduce the tensile strength and elongation at break of the polyester material by even 5\% due to its good resistance to heat. However, high
concentration and particularly boiling temperature cause rapid destruction in the strength of polyester fibers. Generally under concentrated acid conditions, the hydrolysis involved protonation of the in-chain oxygen atom of the ester function followed by reaction with water to produce hydroxyl and carboxyl end groups compounds.

2.1.3.2.4 Resistance to Alkalis

Chemical resistance to alkalis and alkaline substances is not as good as acid resistance. Even hot caustic soda can hydrolyze the fiber surface thus cause the loss of uniformity and tenacity. Polyester fibers just possess adequate resistance to alkalis used in washing process. This behavior is mainly attributed to their high degree of orientation. Under basic conditions at elevated temperature, the hydroxide anion attacks the ester linkages and also produces hydroxyl and carboxyl end groups compounds [12]. The polyester material loses its weight when the polymer chains break down. However, the attack of alkali is limited essentially to the surface of the fiber because it is hard for highly ionized alkaline substances to diffuse inside the nonpolar polymer phase. Thus the diameter of polyester filaments decreases due to the loss of polymer on the surface while the tenacity of the slimmed filaments remains almost unchanged. There are commercially available polyester textiles with silk-like soft feel owing to this controlled alkali hydrolysis of polyester filaments.

2.1.4 The Characteristics of Cationic Dyeable Polyester

Cationic dyeable polyester (CDP) is a special polyester fiber which has undergone a change during polymerization. It is fabricated from PET modified by adding small amount of sodium salt of dimethyl ester of 5-sulfoisophthalic acid (DMS salt), to generate anionic sites that
normal polyester fibers do not have. Figure 4 shows the structure of cationic dyeable polyester. The number of sections containing anionic sites are much less than the number of normal ester sections.

![Structure of cationic dyeable polyester](image)

Figure 4 Structure of cationic dyeable polyester.

This modified polyester possesses similar properties with fibers of normal PET. Having anionic groups it can be dyed with cationic dyes. Also this fiber type was developed to lower the glass transition temperature of the polymer, usually 10 °C lower than normal polyesters, to obtain more segmental mobility and open polymer structure [13], resulting in the dyeing at a lower temperature. This modified polymer is also more readily hydrolyzed and more sensitive to heat setting.

### 2.2 Dyes for polyester

#### 2.2.1 Disperse dyes

Disperse dyes play a dominant role in dyeing polyester fibers. They constitute the second largest sector in the dyeing industry in 2006: 125 thousand tons of disperse dyes were produced, with a value of $900 million [14]. The growth of disperse dyes is inseparable from the development of the new man-made hydrophobic fibers, cellulose acetate. Before the introduction of acetate fibers, almost dyes were applied to substrates from an aqueous dyebath.
However, acetate fibers are very difficult to dye in such way, especially at low temperatures, owing to their hydrophobicity. This problem was solved by creating a fine dispersion of sparingly soluble dyes. The dyes, initially known as ‘cellulose acetate dyes’, were originally synthesized for the dyeing of cellulose acetate fibers and subsequently found to be suitable for the dyeing of a large number of synthetic fibers, particularly polyesters, therefore, in 1953 the Society of Dyers and Colorists renamed them ‘disperse dyes’ [15]. Disperse dyes are also employed for dyeing nylon and acrylic fibers but with limited success, due to the poor fastness properties in the case of nylon and low saturation on acrylic. Other fibers such as polypropylene, are often mentioned in disperse dye patents, but these are generally of academic interest only and are not used for practical applications.

The first ever disperse dye, sulpho ricinoleic acid (SRA) Orange 1, was synthesized by Holland Ellis for British Celanese Ltd in 1923 in dyeing cellulose acetate fibers. In the early stage, these dyes being simple, nitro, azo and anthraquinone dyes were found to have low sublimation fastness and those based on anthraquinone backbone were found to fade by NO\textsubscript{x} gases found in the urban environment [14]. Polyesters and other synthetic fibers required higher dyeing temperature than acetate, which necessitated using dyes with excellent hydrolytic stability over rather wide pH ranges. Polyester dyes also needed resistance to sublimation for fabric pleating, ironing etc. The first tasks of development of suitable disperse dyes for the dyeing of polyester were to improve their sublimation and gas fume fading properties. In the 1950s, textile dye chemists made great advances by introducing additional groups in the dye molecules to increase their molecular weight so that to improve the sublimation fastness, as illustrated in
Table 1, and the deficiency of gas fume fading was rectified by protecting the easily reducible amino groups in the anthraquinone based disperse dyes [16].

Table 1 Improving sublimation fastness of disperse dyes by increasing molecular weight.

<table>
<thead>
<tr>
<th>Original dye with low sublimation fastness</th>
<th>Modified dye with improved sublimation fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="C.I. Disperse Yellow 9" /></td>
<td><img src="image2" alt="C.I. Disperse Yellow 70" /></td>
</tr>
<tr>
<td>C.I. Disperse Orange 30</td>
<td>C.I. Disperse Orange 62</td>
</tr>
<tr>
<td><img src="image3" alt="C.I. Disperse Red 15" /></td>
<td><img src="image4" alt="C.I. Disperse Red 60" /></td>
</tr>
</tbody>
</table>

Subsequently, disperse dyes were developed to meet the specific requirements of polyester, such as ‘alkali clearing’ dyes and the dyes having low thermal-migration and high wash fastness. The alkali clearable dyes are the di-ester-side group containing dyes that could be surface cleared without a hydrosulfite, thereby reducing the pollution of the effluent. They were introduced for the purpose of dyeing polyester cellulosic (PC) blended fabric. These dyes
have also been employed in the discharge printing of polyester fabrics where the dye from the alkali printed portion of the printed design can be easily washed with hot aqueous alkali solution. Figure 5 demonstrates the typical alkali clearing mechanism of a Dispersol PC dye [17].

![Figure 5 Alkaline hydrolysis of Dispersol PC dyes.](image)

In the presence of an alkali the alkoxy carbonyl groups are hydrolyzed to the corresponding carboxylic acids, which give the dye water solubility but little or no substantivity for PET fibers.

2.2.1.1 Classification of disperse dyes

By definition, disperse dyes are nonionic colorants with very limited solubility in water at room temperature. They have substantivity only for hydrophobic fibers [18]. They are usually applied from a fine aqueous dispersion containing some dissolved dye. In order to efficiently diffuse into fibers, the particles of disperse dyes should be as fine as possible comprising low molecular weight molecules in the range of 400-600. The good dispersion stability is an essential requirement to achieve satisfactory dyeing. For this, the particle size of the dye is kept to less than 1 μm [14]. Dyes may always be classified in a variety of ways, some of which are
unique to the particular application category. Disperse dyes are no exception. For example, in the 1970s ICI developed a method for the classification of disperse dyes according to their sublimation fastness and dyeing properties, and divided them into four categories named A to D. Category A dyes have relatively low molecular weight and therefore poor sublimation fastness, but good dyeing properties, whereas category D dyes have high molecular masses and hence desirable sublimation fastness, but somewhat poorer dyeing properties. Category B and C are in the middle of these two extremes. As might be anticipated, a chemical classification by chromophore is very useful to dye chemists but generally the least useful to the dyers. The Colour Index listed around 1,150 disperse dyes in 1992 by chemical class, including but not limited azo, anthraquinone, nitrodiphenylamine, coumarin, methine, aminoketone, quinoline and miscellaneous [16]. In more recent times, dyes are being classified on the basis of end-use, such as automotive fabrics having very high light fastness or dyes for sportswear and heavy-duty work-wear with very high level of wash fastness.

2.2.1.1.1 Azo disperse dye

Azo dyes are defined as compounds containing one or more azo groups, -N=N-, which links two sp2 hybridized carbon atoms, such as benzene, naphthalene, thiazole and so on. Often, these carbons are part of aromatic systems, but this is not always the case. Under normal conditions, azo dyes exist in the stable planar trans-form (Figure 6).

\[ \text{R}_1\text{N=N}_2\text{R}_3 \]

Figure 6 The trans-form of an azo dye.
Azo dyes are by far the most important class and account for more than 50% of the total commercialized disperse dyes in the world [18]. The general method for making an azo dye requires a coupling component and a dizao component. Since these can be adjusted considerably, an enormous range of possible dyes are available, especially as the starting molecules are readily available and cheap. In theory, azo dyes can supply a complete rainbow of colors, from yellow to blue-green and even black hues. However, commercially they tend to supply more yellows, oranges and reds than any other colors.

As mentioned above, in order to facilitate satisfactory dye dispersion, the molecular size of a disperse dye must be kept small. Mono-azo structures are therefore exceptionally important. A typical monoazo disperse dye, aminoazobenzene is of importance in the azo family, which can be represented by the structure shown in Figure 7.

![Figure 7](image)

**Figure 7** General structure of aminoazobenzene disperse dye.

In the structure, X, Y and Z stand for the electron-accepting substituents, and R₁ to R₄ are electron-donating groups. This combination usually creates visible colors from yellows to reds, and in some conditions, blues. In the yellow shade area, molecular size poses no problem since various available coupling components can all be used without making the molecular too large. A good example of simple monoazo structure is Disperse Yellow 3. With the more
bathochromic hues, the requirement for small molecular size can only be met by adding strong donor/powerful auxochrome, such as Disperse Red 72 and Disperse Blue 183. Their structures are shown in Figure 8.

C.I. Disperse Yellow 3

C.I. Disperse Red 72

C.I. Disperse Blue 183

Figure 8 Examples of monoazo disperse dyes.

In these arrangement, electrons are donated from one end of the molecular and attracted on the other end, producing highly polar structures, with a hue bathochromic shift from yellow to red and even blue. In the latter case, the polarity is further increased by incorporating an amide group in the coupling component to reinforce the electron-donating effect.

In addition to benzenoid structures, heterocyclic diazo components are also widely used in the preparation of azo disperse dyes. C.I. Disperse Yellow 8, which uses a simple pyrazolone coupling component, and C.I. Disperse Red 145, which uses a heterocyclic diazo component, are two good examples, and C.I. Disperse Yellow 7 is an example of biazo structure (see Figure 9).
Although there are some deficiencies in azo dyes, such as duller shades, lower light fastness than anthraquinone dyes, and breakdown into carcinogenic amines derived from the cleavage of the azo linkage [19], the cost effectiveness undoubtedly compensates for the drawbacks mentioned above, which makes them still the largest class of synthetic organic dyes.

2.2.1.1.2 Anthraquinone disperse dyes

Anthraquinone dyes are another important type of disperse dyes. Anthraquinone disperse dyes are often more important as reds, violets, blues and blue-greens, thus complementing the azo chemical class [20]. They give brighter colors than azo dyes and can provide excellent light fastness, and wash fastness properties. One the other hand, they are more expensive. Figure 10 is the basic formula of anthraquinone system [14]. The synthesis of anthraquinone is quite
simple, as illustrated in Figure 11, through the reaction of phthalic anhydride with benzene, using aluminum chloride as catalyst, followed by cyclization using $\text{H}_2\text{SO}_4$.

![Reaction diagram]

Figure 10 Anthraquinone numbering system in used disperse dyes.

Figure 11 Synthesis of anthraquinone.

This basic anthraquinone is pale yellow in color. The presence of one or more substituents, such as amino, hydroxyl and methoxy, can lead to significant bathochromic effects so that relatively simple derivatives are commercially important as dyes. Also their positions in the anthraquinone system can be altered in order to achieve a wide range of colors. In general, 1-substituted derivatives of anthraquinone are more bathochromic than the corresponding 2-substituted isomers [21]. This is because that, intramolecular hydrogen bonding is not possible between carbonyl group and the 2-substituted group, and in the 2-substituted series, the bathochromic shift increases with electron-donor power in the sequence: $\text{OH} < \text{OCH}_3 < \text{NHCOCH}_3 < \text{NH}_2 < \text{NHCH}_3 < \text{N(CH}_3)_2$. However in 1-position, the observed bathochromic effect of $\text{NHCH}_3$ is stronger than that of $\text{N(CH}_3)_2$, due to the hydrogen bond formed between
the methylamino group and the adjacent carbonyl group [22]. Moreover, the dimethylamino group is unable to conjugate fully owing to the steric hindrance of bulky substituent, which results in the decrease of intensity. Steric interaction is minimized by rotation of the dimethylamino group out of the plane ring system, as shown in Figure 12.

![Figure 12 Hydrogen bond and steric rotation.](image)

Anthraquinone disperse dyes for cellulose acetate are relatively simple molecules, for example, C.I. Disperse Red 15, C.I. Disperse Violet 4 and C.I. Disperse Blue 3. Dyes for polyesters contain additional hydrophobic substituent groups compared with acetate dyes, such as C.I. Disperse Red 60. Sublimation fastness is improved by adding additional phenoxy ring to C.I. Disperse Red 15. Not many anthraquinone disperse dyes have green colors. C.I. Disperse Green 6:1 is one of the few examples. Heterocyclic ring is often seen in azo disperse dyes, but is rarely seen in anthraquinone system. An interesting exception is C.I. Disperse Blue 60, which possesses a bright blue color.
Anthraquinone dyes are the second most important disperse dyes. Apart from their good fastness properties, they have advantages such as good stability in dyeing and excellent levelling. But they also have the potential to cause pollution problems [23], which make them continuously replaced by other type of disperse dyes.

2.2.1.1.3 Other disperse dye classes

Although azo, anthraquinone disperse dyes are the dominant classes of disperse dyes in terms of market share, other important classes as follows [14]:

Figure 13 Examples of anthraquinone disperse dyes.
- Nitroarylamino disperse dyes
- Coumarin disperse dyes
- Methine disperse dyes
- Naphthostyryl disperse dyes
- Benzodifuranone disperse dyes

2.2.1.2 Properties of disperse dye

Many attempts have been made to investigate the relationships between the chemical structure of a dye and its fastness properties. However, such relationships can be quite complex. The general structure of disperse dyes is small, planar and non-ionic, with attached polar functional groups. The absence of a water solubilizing group makes them hard to dissolve in water. Disperse-dyed polyester generally has good wash fastness because of its low water solubility. Sublimation fastness, is very important due to the use of heat treatment in the finishing of the disperse-dyed polyester fabric. This heat fastness of dyeing is related with molecular size and polarity. Increase in size and/or polarity will tend to increase sublimation fastness as well. However it will reduce the rate of diffusion, which results in relatively poor dyeing properties. Therefore, a compromise between sublimation and dyeing properties has been made. With this in mind, disperse dyes have been classified into types of good dyeing properties but poor sublimation (Class A) through to those with good sublimation but poor dyeing properties (Class D).

Among other properties of dyes, light fastness is one on which most research has been conducted. A close relationship does exist between the chemical structure of a dye and its light
fastness rating. Other factors, including the physical state of the dye within the fiber, the fiber type, environmental factors, and the source and intensity of illumination are also of relevance [19]. The average light fastness of commercial disperse dyes applied to polyesters is highest, followed by acetate, triacetate and then nylon. Light-induced oxidation and reduction reactions are known as the two most important pathways for the fading of dyes. For instance, the fading of azo disperse dye on polyester and acetate (Figure 14) [19], it converses the azo group to an azoxy group.

![Figure 14 Oxidative fading mechanism of azo dye.](image)

The general correlations between monoazo disperse dyes and light fastness behavior can be summarized as follows:

![Figure 15 Typical disperse monoazo system.](image)
Table 2 Relationship between substituent group and light fastness property [20].

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Light fastness</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = Nitro</td>
<td>Poor</td>
<td><img src="image1" alt="Explanation" /></td>
</tr>
<tr>
<td>X = CN, Cl</td>
<td>Good</td>
<td>Light fastness improved by replacing –NO$_2$ with –CN, -Cl and other electron-acceptor groups</td>
</tr>
<tr>
<td>Y = Nitro</td>
<td>Good</td>
<td><img src="image2" alt="Explanation" /></td>
</tr>
<tr>
<td>Z = NHAc</td>
<td>Good</td>
<td><img src="image3" alt="Explanation" /></td>
</tr>
<tr>
<td>$R_1/R_2 = \text{CH}_2\text{CH}_2\text{OH}$</td>
<td>Poor</td>
<td>-CH$_2$CH$_2$OH not stable</td>
</tr>
<tr>
<td>$R_1/R_2 = \text{CH}_2\text{CH}_2\text{CN}$</td>
<td>Good</td>
<td>Stable</td>
</tr>
<tr>
<td>$R_1/R_2 = \text{CH}_2\text{CH}_2\text{OAc}$</td>
<td>Good</td>
<td>Stable</td>
</tr>
</tbody>
</table>

Anthraquinone dyes have better light fastness than most other dye classes. Anthraquinone itself is stable, and thus chemical or physical reactivity is likely to be governed principally by substituent groups attached in the system. A relation between light fastness and different substituted anthraquinone dyes has been achieved by researchers (Table 3) [24].
Table 3 Light fastness values of anthraquinone compounds.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Light Fastness*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-amino</td>
<td>1</td>
</tr>
<tr>
<td>2-N-methylamino</td>
<td>1</td>
</tr>
<tr>
<td>2-hydroxy</td>
<td>1</td>
</tr>
<tr>
<td>2-methoxy</td>
<td>1</td>
</tr>
<tr>
<td>1-amino</td>
<td>4-5</td>
</tr>
<tr>
<td>1-amino-2-hydroxy</td>
<td>4-5</td>
</tr>
<tr>
<td>1,4-diamino</td>
<td>4</td>
</tr>
<tr>
<td>1-amino-4-hydroxy</td>
<td>6</td>
</tr>
<tr>
<td>1-amino-3-carboxy</td>
<td>8</td>
</tr>
<tr>
<td>1-hydroxy</td>
<td>8</td>
</tr>
<tr>
<td>1,4-dihydroxy</td>
<td>8</td>
</tr>
<tr>
<td>1,2-dihydroxy</td>
<td>8</td>
</tr>
</tbody>
</table>

*Scale = 1 (lowest) – 8(highest)

2.2.2 Basic dyes

There are also modified polyesters which can be dyed with basic dyes, but they account for less than 10% of the polyester market. Meanwhile, being dyeable by basic dyes in no way prevents them being dyed with disperse dyes as well. Usually the terms basic dyes and basic dyeable are completely interchangeable with the terms cationic dyes and cationic dyeable.

As the name implies, basic dye molecule has a positive charge [25], unlike most dyes, which have either a negative charge or no charge at all. The word basic refers to bases, as opposed to acids. This class of synthetic dyes act as bases and when dissolved in water, they form a colored cationic moiety, which can react with the anionic sites on the polymer chains.

Basic dyes are salts, usually chlorides, and they are powerful coloring agents. Basic dyes are not used on cotton as the structures are neither planar nor large enough for substantivity. They
can be applied to wool, silk, and sometimes modified polyesters and acrylic fibers [23]. Basic dyes definitely have a lot of advantages [25] like wide shade range, high tinctorial strength, and good brightness. However, they also have limitations during application, such as poor shade stability, very poor light fastness, high acid content, colored backwaters, and low substantivity towards most natural and synthesis fibers making them not as wide spread as disperse and other dyes.

2.3 Dye decolorization methods

Theoretically, many processes can be employed to decolorize polyesters and the treatment methods can be divided into the three categories [26]: physical, chemical and biological methods.

2.3.1 Physical methods

Physical methods such as extraction can be employed to remove the dyes. Extraction, for instance, can remove the dye molecules from textiles using aqueous solutions or organic solvents. However, when the extraction progresses, the dye concentration inside and outside the fibers will reach to a thermodynamic equilibrium. In another words, extraction cannot make the textiles fully colorless, without removing the dyes from the bath continuously. Physical processes such as adsorption and membrane filtration [27] can be used in the removal of dyes that exist in solutions or dispersions. Carbon has been used as an adsorbent for decades. In textile industries, adsorption process using granular activated carbon has regarded as a practical approach to treat the wastewater from dyeing. For instance, granular active carbon was used to absorb methylene blue, Acid Orange 7 and some reactive dyes [28]. Granular activated
carbon [29] is a particularly good adsorbent medium owing to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1,000 square meters. This high surface area permits the accumulation of a large number of contaminant molecules [29]. However, there are several disadvantages of these methods. Firstly, they simply transfer the dye molecules to another phase rather than destroying them. It is also reported that they are effective only when the bath volume is small.

A membrane is a barrier that allows one component of mixture to permeate the membrane freely, while hindering permeation of other components. Membrane filtration process has the ability to clarify, concentrate, and most importantly, to separate dye continuously from aqueous solutions. Membrane technologies are so effective that they can remove all dye types, but utilize significant amount of energy and result in secondary pollution by producing concentrated sludge.

2.3.2 Chemical methods

There are several chemical ways to modify the structure of dye molecules, such as oxidation, reduction, photo-catalytic and ozonation [30]. The most common ones are the first two methods. If the molecular structure of dye were changed, there is a good chance that the new structure would be colorless.

2.3.2.1 Oxidation

In conventional oxidation technologies, hydrogen peroxide and hypochlorite are reported as the widely used oxidation agents. Hydrogen peroxide is widely used in industrial oxidation due to its low environmental impact and cost, and its flexibility for use in different type of
fibers [32]. It is a weak acid and ionizes in water to form HOO\(^-\), which is able to produce more derivatives and is regarded as the active bleaching species.

\[
\text{H}_2\text{O}_2 \xrightarrow{} \text{H}^+ + \text{HOO}^- 
\]

However, it may fail or take extremely long time to decolorize dark hues. This method, therefore, may not generate satisfactory "market white" substrates. Chlorine-containing substances such as alkaline solution of sodium hypochlorite, powder of calcium hypochlorite, chlorine and chlorine dioxide are applicable to bleach cellulosic fabric. In the case of sodium hypochlorite, the species present in the solution can be understood from the following equations:

\[
\text{NaOCl} + \text{H}_2\text{O} \xrightarrow{} \text{Na}^+ + \text{OCl}^- \\
\text{OCl}^- + \text{H}_2\text{O} \xrightarrow{} \text{HOCl} + \text{OH}^-
\]

Even though it is a low cost method and decolorizes color effectively, it often produces hazardous byproducts and generate large amount of solid wastes, which require other costly disposal methods. Due to these reasons, considerable attention had been paid to complete oxidize organic compounds to harmless products by Advanced Oxidation Process (AOP) [33]. The AOP is mainly a UV-driven process, using UV light with an oxidizer such as hydrogen peroxide and/or ozone to generate highly reactive hydroxyl radicals which can attack organic compounds non-selectively with high a reaction rate [34]. Fenton’s reagent is an effective oxidizer [35]. It is a combination of hydrogen peroxide and an iron catalyst and is able to generate free radicals automatically without UV or other energy, which makes Fenton’s reagent more cost effective in comparison with other AOPs. Two equations in Figure 16 [36] present the process of how the hydroxyl radicals are produced. In the second step, the ferric
iron is reduced back to ferrous iron, which indicates that the iron is not consumed and can be recycled after treatment, unless Fe(OH)_3 precipitate is formed.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{H}_2\text{O} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HOO}^+ + \text{H}^+
\end{align*}
\]

Figure 16 Production of hydroxyl radicals in Fenton’s reagent.

2.3.2.2 Reduction

Reduction of dyes is an organic redox reaction [37]. Most reducing agents used in textile applications are compounds that can slowly decompose and release sulfur dioxide under specific conditions [38]. Then the generated sulfur dioxide reacts with dye molecules, not fibers, thus they are safe to be used on nearly all the fibers.

Thiourea dioxide (TUDO) is the diamide of thiocarbonic acid that resembles urea but contains sulfur instead of oxygen [39]. Figure 17 shows the structure of TUDO.

![Thiourea dioxide structure](image)

Figure 17 Thiourea dioxide structure.

It plays an important role in the textile industry as a powerful reducing agent. Its application covers a lot of fields, such as dyeing and printing with vat dyes, discharge printing and stripping. TUDO can remain active under a wide range of alkaline conditions. The reduction treatment of synthetic dyes by TUDO in combination with soda ash and alkali is vast in literature.
Sodium hydrosulfite, also known as sodium dithionite, \( \text{Na}_2\text{S}_2\text{O}_4 \), is an inexpensive and versatile reducing agent [40]. It is stable under dry conditions, but is slowly oxidized by air when in solution. Even with the absence of air, solutions of sodium hydrosulfite decompose. Thus it cannot be stored for a long period of time. After reduction, \( \text{H}_2\text{S} \) is formed as a byproduct, which is very poisonous, corrosive and flammable [41].

2.3.3 Biological methods

Owing to the complex structure of dyes and their molecular design, many dyes are difficult to decolorize and decompose biologically. Most disperse dyes, especially azo dyes are believed very stable and decomposed only at temperature higher than 200°C. Bioaccumulation and biosorption are the two main technologies in biological process, and have already been employed in a large scale to remove dyes in industrial effluents and wastewaters. Bioaccumulation is defined as the phenomenon of uptake of toxicants by living cells; whereas, biosorption can be defined as the passive uptake of toxicants by dead or inactive biological materials [42]. They possess good potential to replace conventional methods for the removal of dyes in aqueous treatment due to their environmentally benign properties, for example, no secondary pollution. Application of laccase enzyme on the two dyes namely C.I. Acid Black 52 and C.I. Acid Blue 113 resulted in biodegradation levels of 92.2 and 94.5%, respectively [42]. Many other azo dyes, such as Reactive Yellow 107, Reactive 198 and Direct Blue 71 have been successfully decolorized by other biological materials [43][42]. However, decolorization of fibers and fabrics are more likely to occur at high temperatures, which will definitely destroy the reactivity of those biological materials [44]. It cannot be readily
employed to remove colors directly from polyesters. In addition, the biological process suffers from low degradation efficiency or even no degradation for some dyes and practical difficulty in continuous process. Therefore, the biological processes so far developed have been relatively ineffective.

2.4. Sodium formaldehyde sulfoxylate

2.4.1 Introduction to sodium formaldehyde sulfoxylate

Sodium formaldehyde sulfoxylate (SFS), is sodium hydroxymethanesulfinate dihydrate, which is represented by the chemical formula HOCH$_2$SO$_2^-$ • Na$^+$ • 2H$_2$O (Figure 18). The salt has many names, sodium bisulfite formaldehyde adduct, formaldehydesulfoxylic acid sodium salt, sodium oxymethanesulfinic acid, etc. The most familiar commercial name is Rongalite [45].

![Figure 18 Chemical structure of sodium formaldehyde sulfoxylate.](image)

SFS contains large, transparent and tubular crystals. It is a strongly hygroscopic substance and should be stored in a dry, cool and dark place. SFS is odorless or possesses a faint leek smell. The loss of purity and hence the reactivity is indicated if it smells like fish. The stability of SFS at various temperatures and under acidic or basic conditions has been studied thoroughly by scientists. In aqueous solution at high temperature, for instance 80°C, SFS was found to decompose and produce sodium sulfite (Na$_2$SO$_3$), sodium sulfide (Na$_2$S), formaldehyde (HCHO), sulfur dioxide (SO$_2$) and hydrogen sulfide (H$_2$S) [46], which decreases the pH of the
solution. Figure 19 shows the decomposition reaction of SFS at 80°C. When SFS was heated at 100 °C, the decomposition was accompanied by an increase in pH due to the production of sodium hydroxide (NaOH).

![Chemical reaction equation]

Figure 19 SFS decomposition reaction at 80 °C.

SFS is readily soluble in water to approximate 600g/L at room temperature, and is an endothermic process. A 10% SFS aqueous solution has a pH of 9-10. It exhibits good stability to alkalis, but is decomposed by acids [47].

Although the toxicological properties of SFS have not been thoroughly reported, it liberates toxic gases (H₂S and SO₂) during application if it were on contact with acid or heated to high temperatures, which would be an environmental concern. The toxic gas may be harmful if absorbed through the skin, cause eye irritation, and may be harmful as well if swallowed or inhaled [45].

2.4.2 Reactivity of sodium formaldehyde sulfoxylate

SFS’s commercial name, rongalite, in French means discharge, and SFS is commonly used as a bleaching agent in the printing and dyeing industry. It is an excellent bleaching agent for some organic compounds owing to its great reducing property. It has been shown that the majority of the reactions involving SFS as the reducing agent occur through cleavage of the C-S bond (Figure 20) and the formation of SO₂⁻ anions of sulfoxylic acid, which exhibits strong
potential to reduce the functional groups of organic compounds without destroying the carbon frame [38].

\[ \text{HOCH}_2\text{SO}_2^- + \text{OH}^- \rightarrow \text{SO}_2^{2-} + \text{HOCH}_2\text{OH} \]

Figure 20 Cleavage of C-S bond of SFS.

There are records [48] available which show SFS is an effective reagent for reduction of some aromatic aldehydes, benzils, ketones and other carbonyl compounds. There has been a debate as to whether reduction of those organic compounds by SFS occurs by initial nucleophilic attack of sulfur dioxide radical anion or by an electron transfer mechanism from \( \text{SO}_2^{2-} \) anion. However, because of large difference in reactivity of aromatic aldehydes and ketones, the dependence on the ring substituents and the reduction under neutral or basic conditions, a nucleophilic and radical mechanism are both likely to occur for the reduction by SFS [48]. The nucleophilic attack of an aromatic aldehyde compound can be summarized in Figure 21. Initial nucleophilic attack could be either \( \text{SO}_2^{2-} \) (Path A) or \( \text{HOCH}_2\text{SO}_2^- \) (Path B) or both.

![Figure 21 Reduction of aromatic aldehyde to alcohol by SFS in aqueous media.](image-url)
SFS is a powerful reducing agent, is inexpensive and commercially available, and can be handled without any special precautions, which make it a great candidate for decolorizing polyesters.

2.5 Characterization of decolorization performance

2.5.1 Whiteness Index

The color “white” is associated with purity, freshness, and cleanliness. White is important to the textile industry for its aesthetic value and for utilitarian purposes. Whiteness is defined as a measure of how closely a surface matches the properties of a perfectly white surface, which in colorimetric terms is defined as a color with the highest luminosity, no hue and no saturation [49]. For the purposes of this standard, the color of such a surface is known as the preferred white. The Whiteness Index (WI) is a number computed by an instrument that indicates the level of whiteness [50]. The higher the WI value, the greater the whiteness of the measured sample. If the preferred white fabric has a high reflectance, then the ideal Whiteness Index for textile material should approach 100. The most commonly used method for computing a whiteness index is CIE (International Commission on Illumination) Whiteness Index. In the CIE measurement system, all colors, including white, can be specified numerically and defined by tristimulus values. CIE WI allows users to identify and compare the level of whiteness of two or more objects. The associated formula, shown in Equation 2, is also recommended by textile associations and is used widely.

\[
\text{WI CIE} = Y + 800 (x_n-x) + 1700 (y_n-y)
\]  

(2)
Where Y, x, y are the luminance factor and chromaticity coordinates of the specimen, and x_n, and y_n are the chromaticity coordinates for the CIE standard illuminant and source used. These values are provided in the Table 4 based on the different illuminant and observer. Whiteness Index can only be calculated for illuminants C, D50 and D65 with 2° or 10° observer. Currently, no additional illuminants are incorporated into the standard.

Table 4 Chromaticity coordinates for the CIE standard illuminant and observer combinations.

<table>
<thead>
<tr>
<th>VALUE</th>
<th>C/2</th>
<th>C/10</th>
<th>D50/2</th>
<th>D50/10</th>
<th>D65/2</th>
<th>D65/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>x_n</td>
<td>0.3101</td>
<td>0.3104</td>
<td>0.3457</td>
<td>0.3477</td>
<td>0.3127</td>
<td>0.3138</td>
</tr>
<tr>
<td>y_n</td>
<td>0.3161</td>
<td>0.3191</td>
<td>0.3585</td>
<td>0.3595</td>
<td>0.3290</td>
<td>0.3310</td>
</tr>
</tbody>
</table>

2.5.2 Color strength

Color strength of a dye is defined as its ability to impart color to other materials. The lower the concentration of a dye required to achieve a defined impression of color that is a given depth of a shade, the greater the color strength of the dye. It depends on the absorption coefficient (K) of colorant, as well as the scattering coefficient (S). Black scatters least and absorbs most, while white scatters most and absorbs least. There is experimental evidence suggesting a linear relationship exists between dye concentration and the absorption and scattering coefficients at specific wavelengths over a fairly large range of concentrations [49]. The overall relationship, known as the Kubelka-Munk function, is shown in equation 3 below:

\[
\frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}}
\]  

(3)

Where R_{\infty} denotes the reflectance of an infinitely thick and opaque layer.
Thus, for example, if one doubles the dye concentration, the values of K and S double consequently. For multiple dyes, the generalized relationship is shown in equation 4 and 5 [51].

\[ K = C_1K_1 + c_2K_2 + c_3K_3 + \cdots + K_s \]  

(4)

\[ S = C_1S_1 + c_2S_2 + c_3S_3 + \cdots + S_s \]  

(5)

And therefore:

\[ \frac{K}{S} = \frac{C_1K_1 + c_2K_2 + c_3K_3 + \cdots + K_s}{C_1S_1 + c_2S_2 + c_3S_3 + \cdots + S_s} \]  

(6)

Where \( c_i \) represents the concentration of the colorant and the subscript \( s \) denotes the substrate before any colorant is added.

The K/S ratio is fairly easy to measure with a reflectance spectrophotometer. It can be used to determine the color strength, which is in turn related to the amount of dye applied. The larger the K/S value of a given sample, the greater is the amount of dye on the surface of the substrate. The K/S ratio may be reported at the maximum reflectance wavelength, denoted as \( (K/S)_{\lambda_{\text{max}}} \).

Alternatively, the value for each wavelength may be summed up over the entire visible spectrum to produce \( \Sigma K/S \). It is important to distinguish between these two values as they will be clearly very different for a given substrate.

2.5.3 Ultraviolet-visible spectrum

An obvious difference between certain compounds is their color. In this respect, our human eyes are functioning as a spectrometer analyzing the colors of solid or liquid surfaces, which are actually determined by the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight or other white light as uniform in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and
infrared (IR) portions of the spectrum (Figure 22). Visible wavelengths cover a range from approximately 400 to 700 nm, among which the longest is red and the shortest is violet. Some common colors in the visible spectrum, in order of decreasing wavelength, which refers to the reflectance wavelength, is bluish green, blue, violet, purple, red, orange, yellow. Visible light absorption is known to all of us. When white light is illuminated at a blue dye for example, a characteristic portion of the mixed wavelengths is absorbed, leaving the blue light to be reflected. The remaining blue light is the complementary color to the wavelengths absorbed.

![Figure 22 Three components of white light.](image)

Therefore, UV-visible spectrophotometer can be used to measure the absorbance of ultra violet or visible light by a sample [52]. The relationship between the wavelength absorbed, color absorbed and the color seen to us is illustrated in Table 5 [20].
A schematic diagram of the components of a typical spectrophotometer is shown in Figure 23. The function of this instrument is quite straightforward. A beam of light from a visible and/or ultraviolet light source is separated into its component wavelengths by a filter, usually a prism or diffraction grating. Each monochromatic beam in turn is split into two equal intensity beams by a half-mirrored device. One beam passes through a small transparent cuvette containing a solution of analyte. The other beam, the reference, passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. Over a short period of time, the spectrophotometer automatically scans all the component wavelengths in the manner described [52]. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 700 nm.

### Table 5 Absorption of visible light and color seen.

<table>
<thead>
<tr>
<th>Wavelength Absorbed (nm)</th>
<th>Color Absorbed</th>
<th>Color Seen</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-435</td>
<td>Violet</td>
<td>Yellow-Green</td>
</tr>
<tr>
<td>435-480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480-490</td>
<td>Green-Blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490-500</td>
<td>Blue-Green</td>
<td>Red</td>
</tr>
<tr>
<td>500-560</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>560-580</td>
<td>Yellow-Green</td>
<td>Violet</td>
</tr>
<tr>
<td>580-595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>595-605</td>
<td>Orange</td>
<td>Green-Blue</td>
</tr>
<tr>
<td>605-700</td>
<td>Red</td>
<td>Blue-Green</td>
</tr>
</tbody>
</table>
Figure 23 Components of a UV-visible spectrophotometer.

The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$, while the intensity of the sample beam is defined as $I$. The ratio $I/I_0$ is called the transmittance, denoted by $T$. The absorbance, $A$, is based on the transmittance. Their relationship can be described by the following equation:

$$ A = \log T $$

The absorption of light by a dye in solution is directly proportional to its concentration; i.e., the greater the concentration of the dye, the greater the amount of light is absorbed. The equation for the absorption is known as Beer’s Law or Beer-Lambert Law, which is:

$$ A = \varepsilon bc $$
Where $A$ is the observed absorption, $b$ is the path length of the sample cell, which is normally 1 cm, $c$ is the concentration of the sample, and $\varepsilon$ is the absorptivity or molar extinction coefficient.

Typical $\varepsilon$ values for mono-substituted anthraquinone disperse dyes are in the range of 4,000-7,000, for di-substituted anthraquinone disperse dyes are about 10,000-17,000 [53].

2.5.4 Intrinsic viscosity and molecular weight

Viscosity is an internal property of a fluid that causes resistance to flow. The viscosity of a polymer based fluid is important for a number of reasons, including its ability to give a feel for the degree of polymerization and an indication of the extent of polymer degradation. Intrinsic viscosity is measured from the flow time of a solution through a simple glass capillary. The intrinsic viscosity as measured from a dilute solution of macromolecules contains information on the macromolecular shape, flexibility, and molar mass of macromolecules. Usually expressed in dl/g, it is defined as the reduced specific viscosity in the limit of “infinite dilution” or zero concentration as shown in equation 9 [11].

$$IV = \lim_{c \to 0} \frac{\eta - \eta_0}{c \times \eta_0}$$  \hspace{1cm} (9)

where $c$ is the concentration of the polymeric solution in g/dl, $\eta$ is the viscosity of the solution at concentration $c$, and $\eta_0$ is the viscosity of the solvent.

The most useful type of viscometer for determining intrinsic viscosity is the Ubbelohde viscometer, illustrated in Figure 24. It is a U-shape piece of glassware with a reservoir on one side and a measuring bulb with a capillary on the other side. A liquid is introduced into the
reservoir then sucked through the capillary and measuring bulb. The liquid is allowed to travel back through the measuring bulb and the time it takes for the liquid to pass through two calibrated marks is a measure of viscosity. The Ubbelohde device [54] has a third arm extending from the end of the capillary and open to the atmosphere, which ensures that the only pressure difference between the top of the bulb and the bottom of the capillary is that due to the hydrostatic pressure--i.e., the weight of the liquid. Such a viscometer is also useful in other experiments, for example, checking the stability of a polymer solution, where one is only interested in measuring a change in the flow time.

Figure 24 Ubbelohde viscometer.

Capillary viscometry is conceptually simple [55]: the time it takes a volume of polymer solution to flow ($t_{soln}$) through a thin capillary is compared to the time for a solvent flow ($t_{solvent}$). The relative viscosity is defined to be the ratio $\eta_{soln}/\eta_{solvent}$. For most polymer
solutions at the concentrations of interest, $\rho_{\text{soln}} / \rho_{\text{solvent}} \approx 1$. Thus, to a very good approximation, the relative viscosity is a simple time ratio:

$$\eta_{rel} = t_{\text{soln}} / t_{\text{solvent}}$$

(10)

Another concept is specific viscosity, which is defined to be the fractional change in viscosity upon addition of polymer:

$$\eta_{sp} = \frac{\eta_{\text{soln}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$$

(11)

Both $\eta_{rel}$ and $\eta_{sp}$ depend on the polymer concentration. In order to extract the “intrinsic” properties of the polymer chain itself, we must extrapolate to zero concentration. Measuring at zero concentration ($c=0$) would be useless, but this concept of extrapolating to $c=0$ is very important in polymer characterization and in thermodynamics generally. Both plots have the same intercept, which is called $[\eta]$, the intrinsic viscosity.

The relation between the average molecular weight and intrinsic viscosity has been discussed early in terms of the Mark-Houwink-Sakurada function (equation 1, page 9).

Once $[\eta]$ is known, it is related to molecular weight through two constants, K and a. The value of constant a depends on the polymer-solvent pair and on temperature. These constants must have been previously determined by a calibration experiment or from the handbook of polymer science. Once K and a are known, the measurement of $[\eta]$ on a polymer of unknown molecular weight can be used to calculate the molecular weight.

Polyester is the most widely used fiber in textiles, owing to its unique physical and chemical properties. It is not only used alone as a textile fiber, but also blended with other fibers to enhance the look and durability of the fabric. It is blended with cotton to aid stain and wrinkle
resistance, and blended with wool to aid wrinkle resistance [21]. Thus, polyester dominates the synthetic fiber market at 77 percent, followed by nylon with 12.9%, acrylic with 8.6% and other fibers making 1.5% [56]. Consumption of polyester staple fiber during 2000-2006 witnessed an average annual increase of 5.3%, and in 2006 it jumped up to 11.4%. The approximate global annual production of polyester fiber was around 36 million tons in 2011 [57]. Most of it was dyed by disperse dyes and used in the manufacturing of all kinds of clothes and home furnishings. However, such huge amount of colored polyester has highly limited recycling systems, due to the lack of efficient and environmentally responsible polyester decolorization methods.

2.6 Research project

With the above literature survey in mind, this study involved establishing a method for using the reducing agent sodium formaldehyde sulfoxylate (SFS) to decolorize PET. The goal was to achieve high Whiteness Index and low K/S values, without degrading the fiber. This reduction method was studied in detail with the influence of each process parameter investigated separately. To optimize the concentration of SFS, treatment temperature, reducing time, liquor ratio and the ratio of water to acetone in the bath, were varied in a series of control experiments. The optimized recipe was applied to laboratory dyed PET fabrics and commercial PET garment fabrics. The Whiteness Index, color strength, intrinsic viscosity and number average molecular weight were determined by corresponding measurements.
Decolorization experiments in this research were conducted on some commercial garment fabrics as well as laboratory-dyed fabrics. Dyes used in this work are listed in the Table 6, including the sources from which the dyes were obtained.

Table 6 C.I. Names, structures and sources of dyes used in this study.

<table>
<thead>
<tr>
<th>Color Index name</th>
<th>Chemical Class</th>
<th>Structure</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse Orange 30</td>
<td>Azo</td>
<td><img src="image" alt="Structure" /></td>
<td>Ciba Specialty Chemicals</td>
</tr>
<tr>
<td>Disperse Blue 79</td>
<td>Azo</td>
<td><img src="image" alt="Structure" /></td>
<td>Huntsman International</td>
</tr>
<tr>
<td>Disperse Yellow 114</td>
<td>Azo</td>
<td><img src="image" alt="Structure" /></td>
<td>Huntsman International</td>
</tr>
<tr>
<td>Disperse Yellow 42</td>
<td>Nitro</td>
<td><img src="image" alt="Structure" /></td>
<td>M. Dohmen USA Inc.</td>
</tr>
<tr>
<td>Disperse Yellow 86</td>
<td>Nitro</td>
<td><img src="image" alt="Structure" /></td>
<td>M. Dohmen USA Inc.</td>
</tr>
</tbody>
</table>
Table 6 C.I. Names, structures and sources of dyes used in this study (continued).

<table>
<thead>
<tr>
<th>Dye</th>
<th>C.I. Name</th>
<th>Structure</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse Red 60</td>
<td>Anthraquinone</td>
<td><img src="structure1.png" alt="Anthraquinone Structure" /></td>
<td>Huntsman International</td>
</tr>
<tr>
<td>Disperse Blue 56</td>
<td>Anthraquinone</td>
<td><img src="structure2.png" alt="Anthraquinone Structure" /></td>
<td>Huntsman International</td>
</tr>
<tr>
<td>Disperse Blue 60</td>
<td>Anthraquinone</td>
<td><img src="structure3.png" alt="Anthraquinone Structure" /></td>
<td>Huntsman International</td>
</tr>
<tr>
<td>Disperse Yellow 54</td>
<td>Quinoline</td>
<td><img src="structure4.png" alt="Quinoline Structure" /></td>
<td>Dystar</td>
</tr>
<tr>
<td>Basic Yellow 28</td>
<td>Methine</td>
<td><img src="structure5.png" alt="Methine Structure" /></td>
<td>Dystar</td>
</tr>
</tbody>
</table>
Chapter 3 Experimental methods and procedures

3.1 Materials

3.1.1 Chemicals

Relevant information such as name and chemical constitution of materials and chemicals, except for dyes used in this work are listed in Table 7. Three types of polyester fabrics are used, two of which, colored garments and white cationic dyeable polyesters, were donated by Nike, Inc. (Beaverton, OR, USA). The rest was white, pre-scoured 100% polyester warp knit fabric donated by Guilford, Inc. (Kenansville, NC, USA). Sodium formaldehyde sulfoxylate dihydrate, a white powder, purchased from Arcos Organics.

3.1.2 Instrumentation

Both dyeing and decolorization processes were conducted in an Ahiba Spectradye Plus laboratory-scale dyeing machine. Infrared heating and water cooling made it possible for the machine to control dyeing or decolorization carefully. Process parameters such as temperature, rotation speed and treatment time were regulated and monitored constantly. Colorimetric assessments of samples were conducted using a Spectraflash SF 600X Datacolor Reflectance Spectrophotometer equipped with iMatch software from X-Rite. With the aid of this software, parameters such as L* a* b* color scale and tristimulus values were measured. Color strength and CIE Whiteness Index were determined through the software. An HP/Agilent 8453 UV-Visible Spectrophotometer was used to measure the amount of dyes in the solution after SFS treatment.
Table 7 Materials and chemicals used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester fabric</td>
<td>Colored polyester fabrics from commercial Nike garments (Yellow, Blue, Grey, Red, Black, and Green)</td>
<td>Nike, Inc.</td>
</tr>
<tr>
<td></td>
<td>White, 100% polyester warp knit fabric, 353g/m²</td>
<td>Guilford, Inc.</td>
</tr>
<tr>
<td></td>
<td>White, 100% Cationic dyeable polyester, 153g/m²</td>
<td>Nike, Inc.</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>Sodium formaldehyde sulfoxylate dihydrate, 98%</td>
<td>Arcos Organics</td>
</tr>
<tr>
<td></td>
<td>Sodium hydrosulfite</td>
<td>Marlin Company, Inc.</td>
</tr>
<tr>
<td>Alkali</td>
<td>Sodium hydroxide, 37.6% aqueous solution</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Acid</td>
<td>Acetic acid, 90% aqueous solution</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td></td>
<td>Citric acid, powder</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Salt</td>
<td>Sodium sulfate, &gt; 99%, Na₂SO₄</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Dispersing agent (Novadye NT)</td>
<td>Boehme Filatex, Inc.</td>
</tr>
<tr>
<td></td>
<td>Apollo Scour SDRS</td>
<td>Apollo Chemical</td>
</tr>
<tr>
<td></td>
<td>Antifoaming agent</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Nonionic detergent</td>
<td>--</td>
</tr>
<tr>
<td>Fabric solvent medium</td>
<td>o-Chlorophenol</td>
<td>Arcos Organics</td>
</tr>
</tbody>
</table>
3.2 Dyeing experiments

3.2.1 Dyeing of polyester fabrics with high volume disperse dyes

White, pre-scoured polyester knit fabrics were cut into 7.5g pieces. Stock solutions (1g/L) of disperse dyes were prepared, with the addition of dispersing agent Novadye NT 9 (1 mL). The dyebath consisted of tap water, stock dye solution, and glacial acetic acid (50 μL). The liquor ratio was 20:1. The amount of stock dye solution was varied to give the target percent dye on-weight-of-fiber (%owf). The polyester samples were dyed in a DataColor Ahiba Spectradye Plus dyeing machine in a 150-mL dyebath. The dyebath temperature was increased from room temperature to 130°C at a ramp rate of 4°C/min over 30 min. The dyebath was held at 130°C for 30 min and allowed to cool for 30 min.

Tap water (15 L) was added to a kettle and heated to 80°C. Na₂S₂O₄ (2 g/L), NaOH (2 g/L), and Apollo Scour SDRS surfactant (2 g/L) were added to the kettle. The dyed polyester fabric samples were added to the kettle and agitated for 15 min. The fabric swatches were removed, and the kettle was drained and refilled with 15 L of fresh water. Glacial acetic acid (2 g/L) was added to the bath and the fabrics were returned to the kettle and agitated for 5 min, removed, and allowed to air-dry.

3.2.2 Dyeing of cationic dyeable polyester with basic dyes

Basic dye (1g/L) was dissolved in tap water at 60°C with 1g/L of acetic acid and used to dye 10g fabric samples. Dyebath consisted of water, stock solution (75 mL), antifoaming agent (0.5g/L), Na₂SO₄ (6g/L), and dispersing agent Novadye NT (1g/L). Liquor ratio was 20:1. The pH value was controlled at 4~5 by acetic acid. The temperature of dyebath was raised to 70°C.
at a ramp rate of 1°C/min. From 70°C to 85°C, the temperature was increased slowly by the rate of 0.5°C/min. The dyebath was held at 85°C for 10 min, then raised to 120°C at 0.6°C/min. The dyebath was held for another 45 min and allowed to cool to 70°C at 0.5°C/min. After dyeing, the dyed samples were rinsed several times with 2 g/L non-ionic detergent at 60-70°C.

3.3 Preliminary decolorization experiments

3.3.1 Decolorization of dye solutions/dispersions

Stock solutions were prepared using disperse Blue 56, Blue 60, Yellow 114, Yellow 42 and Yellow 86 at a concentration of 1g/L. Each stock solution (50mL) was mixed with sodium formaldehyde sulfoxylate (1.25g) in beakers, and pH was adjusted to 4.5 by citric acid (0.1g). The temperature of the solution was raised to 85°C and held for 30 min. After treatment, the solutions were measured using a UV-Visible spectrophotometer to determine the concentration of dye left in the solution.

3.3.2 Decolorization of industrial garment fabrics and laboratory-dyed fabrics

The fabric was cut into 1g pieces. Reducing agent SFS (4g) was dissolved in 1:1 water/acetone (100mL). The pH was adjusted to 4.5 by adding citric acid (0.1g). The bath was heated to 100°C at the ramp rate of 4°C/min and held for 60 min. The bath was cooled, and the fabric was rinsed with room temperature water, and allowed to air-dry.

3.4 Optimization of experiments

3.4.1 Design of experiments

The Design of Experiments (DOE) was conducted using JMP Pro 11 software. Temperature, time, ratio of water to acetone, liquor ratio, and concentration of SFS were taken into account
in the experimental design. Each variation was set at two levels, i.e., high level and low level. The temperature at its high level was 120°C and low level was 80°C. A full factorial design of experiment made through the software JMP is shown in Table 8.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Water: Acetone</th>
<th>L.R.</th>
<th>[SFS] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>30</td>
<td>1:2</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>30</td>
<td>1:2</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>30</td>
<td>1:1</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>30</td>
<td>1:1</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>30</td>
<td>1:1</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>30</td>
<td>1:2</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>30</td>
<td>1:2</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>30</td>
<td>1:2</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>80</td>
<td>60</td>
<td>1:2</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>60</td>
<td>1:2</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>60</td>
<td>1:1</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>80</td>
<td>60</td>
<td>1:1</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>120</td>
<td>60</td>
<td>1:2</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>120</td>
<td>60</td>
<td>1:2</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>15</td>
<td>120</td>
<td>60</td>
<td>1:1</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>16</td>
<td>120</td>
<td>60</td>
<td>1:1</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>

The decolorization process was conducted in an Ahiba Spectradye Plus dyeing machine.

3.4.2 Optimization by control experiments

Five series of controlled experiments were conducted. Fabric used in these controlled experiments was the commercial dark grey cloth.
Series 1: liquor ratio (50:1), concentration of SFS (40g/L), ratio of water to acetone (1:1) and temperature (120°C) were controlled, and the treatment time was varied from 5, 10, 15, 20, 30, 40, 50, to 60 min.

Series 2: liquor ratio (50:1), treatment time (30 min), concentration of SFS (40g/L) and temperature (110°C) were controlled, and the ratio of water to acetone was varied from 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 to 1:4.

Series 3: liquor ratio (50:1), treatment time (30 min), ratio of water to acetone (1:2) and temperature (110°C) were controlled, and the concentration of SFS was varied from 5, 10, 15, 20, 25, 30, 35, to 40 g/L.

Series 4: liquor ratio (50:1), treatment time (30min), ratio of water to acetone (1:2) and concentration of SFS (10g/L) was controlled, and the temperature was varied from 70, 80, 90, 100, 105, to 110°C.

Series 5: treatment time (30 min), ratio of water to acetone (1:2), temperature (110°C) and concentration of SFS (10g/L) were controlled, and the liquor ratio was varied from 1:10, 1:20, 1:30, 1:40 to 1:50.

Optimized method was achieved: treatment time (30min), ratio of water to acetone (1:2), concentration of SFS (10g/L), temperature (100 °C), and liquor ratio (1:50).

3.4.3 Decolorization of other fabrics using optimized method

The optimized method was employed to cationic dyeable PET dyed using 6 randomly selected high volume disperse dyes and 1 high volume basic dye. Disperse dyes were applied at 1% (owf) using two azo (Disperse Orange 30, Disperse Blue 79), two anthraquinone (Disperse
Red 60, Disperse Blue 56), and two nitro dyes (Disperse Yellow 42, Disperse Yellow 86). Basic Yellow 28 was employed at 0.75% (owf). Fabrics were cut into 1g pieces. Water and acetone medium was prepared at the ratio of 1:2. Reducing agent SFS (0.5g) was dissolved in the water/acetone medium (50mL). The bath was heated to 110°C at the ramp rate of 4°C/min and held for 30 min. The bath was cooled, and the fabrics were rinsed with room temperature water, and allowed to air-dry.

3.4.4. Reuse of decolorization bath
The decolorization process was the optimized method. However at the end of each treatment cycle, the fabric was removed and squeezed thoroughly. To the bath that remained, 10 g/L of SFS was added and a new decolorization was conducted.

3.5 Measurement of decolorized fabrics
3.5.1 Color strength
A calibrated Datacolor Spectraflash 600X Reflectance Spectrophotometer with iMatch software from X-Rite was used to measure the K/S values of the PET fabrics following AATCC Evaluation Procedure 6 [59]. The K/S value of each sample was calculated by adding the K/S values of each 10 nm from the wavelength of 400 nm to 700 nm. The software was set to use illuminant D65 with the UV light included, and the CIE 10-degree supplemental standard observer. The sample being tested was folded twice. Each sample was measured two times by rotating the sample at 90 degrees between each measurement. The average value was recorded.
3.5.2 Whiteness Index

A calibrated Datacolor Spectraflash 600X Reflectance Spectrophotometer with iMatch software from X-Rite was used to measure the CIE Whiteness Index of the PET fabrics following AATCC Test Method 110 [60].

The software was set to use illuminant D65 with the UV light included, and the CIE 10-degree supplemental standard observer. For each sample, four layers of fabric were measured and each sample was measured two times by rotating the sample at 90 degrees between each measurement. The average value was recorded.

3.5.3 Intrinsic viscosity and calculation of molecular weight

The measurement of intrinsic viscosity using Ubbelohde viscometer was made at room temperature. PET (0.2 g) was dissolved in 20 mL of o-chlorophenol at 76.5 °C over 40 min. The solution was cooled to room temperature. The flow time for pure o-chlorophenol and the fabric solution to pass the indicator lines were determined and recorded. The solution was diluted 6 times and the flow time for each concentration was measured. An $\eta_{sp} / c$ vs. $c$ plot was drawn and the intercept [$\eta$] was obtained. The calculation of the molecular weight was based on the Mark-Houwink equation. The value of $K$ was 0.0372 mL/g and the value of $a$ was 0.73 from polymer data handbook [58].
Chapter 4 Results and discussion

4.1 Preliminary decolorization experiments

4.1.1 Decolorization of solutions

In the initial studies, solutions of five disperse dyes with three types of chromophores (2 anthraquinone, 1 azo, and 2 nitro) were treated with SFS. Figures 25 and 26 show the five dye solutions/dispersions obtained before and after decolorization using SFS at 85°C.

![Figure 25](image1)
Figure 25 Disperse dye solutions before SFS treatment.

![Figure 26](image2)
Figure 26 Disperse dye solution after SFS treatment for 30 min at 85°C.
The pictures show that the color of dye solutions were significantly changed by SFS treatment, but the two anthraquinone dyes (Disperse Blue 56 and Disperse Blue 60) were not completely decolorized; whereas the azo dye (Disperse Yellow 114) and two nitro dyes (Disperse Yellow 42 and Yellow 86) were almost totally decolorized. The color changes were monitored by UV-Visible spectroscopy. The absorption band reduced gradually as time increased. For example, results from Disperse Blue 56 are shown in Figure 27. In addition to a decrease in intensity of the maximum absorbance wavelength (λ\text{max}), the color of the solution underwent a considerable hypsochromic shift, from 630 nm to 525 nm.

![Figure 27 UV-Visible spectra of Disperse Blue 56 after different SFS treatment times.](image-url)
4.1.2 Decolorization of commercial and laboratory-dyed fabrics

The initial decolorization of PET fibers were conducted in water/acetone medium. These experiments were conducted on randomly selected commercial athletic wear fabrics, for which the percent dye on-weight-of-fiber was unknown, and dyed PET samples, which were prepared using high volume disperse dyes from our laboratory.

4.1.2.1 Commercial athletic wear fabrics

Results from SFS decolorization of commercial fabrics are shown in Figure 28. Kebelka-Munk (K/S) values were measured to characterize color remaining on treated fabrics. In these results, the treated fabrics possessed only a faint amount of their original color, which caused low CIE Whiteness Index values. That is why K/S values were measured instead of whiteness indexes. The color strength of each sample was measured before and after treatment. Table 9 presents the corresponding K/S values.

Figure 28 Commercial PET fabrics before and after SFS (40g/L) treatment in acetone/water (1:1) at 100 °C.
The fluorescent yellow sample became slightly grey after SFS treatment. The grey and blue samples became yellowish white. The black fabric was also well decolorized and became off-white. Decolorization of the red sample was not as effective as others, there was a red stain on the fabric. The green sample was bleached efficiently and came to be nearly white.

Table 9 K/S values of each commercial PET fabrics before and after SFS (40g/L) treatment in acetone/water (1:1) at 100 °C.

<table>
<thead>
<tr>
<th>Fabric Color</th>
<th>K/S value</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>53.57</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>Grey</td>
<td>13.22</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>41.81</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>532.63</td>
<td>6.08</td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td>240.63</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>220.66</td>
<td>1.91</td>
<td></td>
</tr>
</tbody>
</table>

The untreated samples were all deeply dyed, which was reflected by their high K/S values, except for the grey one. After decolorization, their colors were reduced dramatically and only a small amount of color retained on the fabric. Both from the perceptual assessment of these samples and statistic measurement of K/S values, it was clear that SFS decolorization is a promising method for treating dyed fabrics as well as dye solutions, since most of these fabrics and solutions had been essentially decolorized.
4.1.2.2 Laboratory-dyed fabrics

In this part of the study, standard PET fabric dyed by some high volume disperse dyes at different shade depths was used. Azo, anthraquinone, and quinoline dyes were randomly selected, namely, Disperse Orange 30, Disperse Blue 60 and Disperse Yellow 54. The decolorization recipe was the same as the one used to decolorize the commercial athletic fabrics. The %owf levels were 0.125, 0.25, 0.5, 1.0, and 2.0. Pictures of the decolorization results are shown in Figure 29. Table 10 contains the K/S values of untreated and SFS-treated fabrics.

Figure 29 Laboratory-dyed PET fabrics before and after SFS (40g/L) treatment in acetone/water (1:1) at 100°C.
The Disperse Orange 30 and Disperse Blue 60 dyed PET fabrics were essentially decolorized.
When %owf was 0.125, Disperse Orange 30 dyed fabric became white. The whiteness of the
decolorized fabrics decreased as the shade depths increased. When %owf was 2.0, the treated
orange and blue samples possessed a small amount of their initial color. But, with respect to
the Disperse Yellow 54, it was very hard to decolorize even at low %owf levels. Therefore,
among the three selected dyes, the SFS decolorization performance on Disperse Yellow 54
was the worse, and the Disperse Orange 30 and Disperse Blue 60 were comparable.

Table 10 K/S values of PET fabrics before and after treated with SFS (40g/L) in
acetone/water (1:1) at 100 °C.

<table>
<thead>
<tr>
<th>Shade Depths (%owf)</th>
<th>K/S value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Orange 30</td>
</tr>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>0.125</td>
<td>31.78</td>
</tr>
<tr>
<td>0.25</td>
<td>53.52</td>
</tr>
<tr>
<td>0.5</td>
<td>109.00</td>
</tr>
<tr>
<td>1.0</td>
<td>204.82</td>
</tr>
<tr>
<td>2.0</td>
<td>297.41</td>
</tr>
</tbody>
</table>

The decolorization results indicated that fabrics with shade depths ≥ 1% were hard to
decolorize. Also the K/S values of treated samples correlated with the visual assessment
(Figure 29). By comparing the results from this small group of known disperse dyes on PET, it is clear that the effectiveness of SFS is related to the disperse dye structure. Although azo and anthraquinone dyes appear to be easier to decolorize than a quinoline dye, the initial studies from SFS treatment on commercial and laboratory-dyed fabrics suggested that this process was a feasible approach to removing a broad range of disperse dyes from PET.

4.2 Optimization of experiments

If the goal was to efficiently decolorize polyesters so that they can be used directly as recycled PET (rePETe), the whiteness achieved in the initial studies may require improvement. To achieve more efficient removal of all commercially used disperse dyes, further optimization of the SFS decolorization method was investigated.

4.2.1 Screening design of experiments

Screening design is among the most popular designs for industrial experimentation. It is typically used in the initial stages to examine many factors and identify those that have the greatest effect on the response. In this case, to investigate the most important parameter(s) that can affect disperse dye decolorization performance significantly, a screening design of 5 factors with 2 levels was conducted: temperature, liquor ratio, ratio of water to acetone, SFS concentration, and time. Factors and levels are presented in Table 11.
Table 11 Factors and levels for screening design.

<table>
<thead>
<tr>
<th>Factors</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>t (min)</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>L.R.</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Water: Acetone</td>
<td>1:1</td>
<td>1:2</td>
</tr>
<tr>
<td>[SFS] (g/L)</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

The design consisted of 16 runs, which were only a fraction of the possible combinations of factor levels. All the decolorizations employed PET fabrics (Figure 30) dyed by Disperse Blue 60, which belongs to the anthraquinone class, at a deep shade (%owf=2.0). In preliminary decolorization experiments, solutions of Disperse Blue 60 were the hardest to decolorize among the selected 5 dyes. If optimized SFS method could decolorize Disperse Blue 60 successfully, there was high possibility that other disperse dyes could be decolorized thoroughly as well. Figure 31 shows samples obtained after 16 treatment combinations that were listed early in Table 8.

Figure 30 PET fabric dyed by Disperse Blue 60 at 2% (owf).
The first and third rows in Figure 31 are fabric samples treated at 80 °C, and the second and fourth rows are fabrics at 120 °C with different liquor ratio, ratio of water to acetone, concentration of SFS, and treatment time combinations. Unfortunately, regardless of the temperature level, the deep blue fabrics could not be fully decolorized. As shown in Figure 31, 8 fabrics at 80 °C remained blue and 8 at 120 °C were yellow. In statistical analysis, dL, which was defined as the differences between the lightness of treated samples and original blue sample, was set as the response. Figure 32 is a sorted parameter estimates report. It includes a bar chart of the individual effects embedded in a table of parameter estimates. The last column of the table has the p-value for each effect. Note that temperature and ratio of water to acetone
have been highlighted, which is because their related p-values are less than the default value (0.05), indicating that these two factors have the greatest influence on the response.

![Sorted Parameter Estimates](image)

Figure 32 Statistical analysis of sorted parameter estimates.

The initial decolorization studies involving laboratory-dyed fabric showed that SFS was able to decolorize the Disperse Blue 60 dyed PET effectively (second column in Figure 29). However in this set of DOE, the best result involved converting PET fabric to yellow, perhaps because the combinations of each parameter were different from the initial experiment in solution. For example, the highest level of liquor ratio used in DOE was 40, whereas in preliminary experiments it was 100. Thus control experiments are needed to establish the influence of each parameters.
4.2.2 Control experiments

There were 6 factors (temperature, ratio of water to acetone, liquor ratio, concentration of SFS, time and pH) of interest at the beginning of this study. Most of them could influence the decolorization results to some extent. Based on the mechanism of SFS decolorization, there are two ways to activate SFS and generate the reactive species. One is high temperature the other was low pH. The temperature in these experiments is high enough to activate SFS, thus pH was excluded in control experiments. In this part of the study, grey fabrics from commercial sportswear were used. Figure 33 shows what the dark grey fabric looked like before treatment.

![Figure 33 Dark grey commercial PET fabric used in control experiments.](image)

4.2.2.1 The effect of treatment time

To determine the relationship between treatment time and decolorization performance, a series of experiments at different treatment times were conducted. Temperature, ratio of water to acetone, concentration of SFS and liquor ratio were kept constant. After SFS treatment, the K/S values of the treated samples were measured in duplicate. Results are shown in Table 12 and visualized by a graph in Figure 34. Figure 35 shows photographs of PET fabrics from the
commercial sportswear, illustrating the effects of treatment time on decolorization performance.

Table 12 K/S value Vs time for dark grey commercial PET fabric after SFS (40g/L) treatment in acetone/water (1:1) at 120 °C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/S value</td>
<td>245.63</td>
<td>12.26</td>
<td>3.45</td>
<td>1.22</td>
<td>0.88</td>
<td>0.67</td>
<td>0.4</td>
<td>0.39</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figure 34 Graph of K/S value Vs time for dark grey commercial PET fabrics after SFS (40g/L) treatment in acetone/water (1:1) at 120 °C.
Figure 35 PET fabrics showing the effect of treatment time on decolorization of dark grey commercial sportswear using SFS (40g/L) at 120 °C.

From these figures it can be seen that the sample treated for 30 min had comparable decolorization level to the one treated for 60 min. Regarding samples treated for 15 and 20 min, most colors was removed. To help establish the lower limit of the treatment time, 5 min and 10 min SFS treatments were considered. However, from the K/S values and photographs shown in Figure 35, it is clear that more color persisted at both time intervals.

4.2.2.2 The effect of water to acetone ratio

The general treatment procedures were the same as used to investigate the effect of treatment time, except for using baths of different water to acetone levels, and the temperature was lowered to 110°C. The boiling points of water and acetone are 100°C and 56°C, respectively. When the beaker was heated to 120°C, the high pressure inside beaker led to an explosion. Respecting the danger of explosion, the treatment temperature in this case was lowered to 110°C.
K/S values were measured and are summarized in Table 13 and Figure 36. Figure 37 contains pictures of PET fabrics treated at different water/acetone ratios.

Table 13 K/S value Vs different water: acetone levels for commercial PET fabric after SFS (40g/L) treatment at 110 °C for 30 min.

<table>
<thead>
<tr>
<th>Water: Acetone</th>
<th>4:1</th>
<th>3:1</th>
<th>2:1</th>
<th>1:1</th>
<th>1:2</th>
<th>1:3</th>
<th>1:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/S value</td>
<td>19.62</td>
<td>12.42</td>
<td>7.39</td>
<td>4.08</td>
<td>2.76</td>
<td>4.39</td>
<td>3.77</td>
</tr>
</tbody>
</table>

Figure 36 Graph of K/S value Vs water: acetone ratio for dark grey commercial PET fabric after SFS (40g/L) treatment at 110 °C for 30 min.
The results showed decolorization took place in all media but higher ratio of water to acetone (4:1 and 3:1) had a negative effect on decolorization efficiency. It can be easily explained that higher proportion of water, is unfavorable for the extraction of sparingly water soluble disperse dyes from PET fabric to the medium. However, significantly increasing the amount of organic solvent (acetone) reduced the decolorization efficiency as well. This is because SFS is only soluble in water, not in acetone. Solubility of reducing agent decreases as acetone content increases, which results in the decrease in decolorization performance. In summary, the most acceptable decolorization resulted when the ratio of water to acetone was 1 to 2.

4.2.2.3 The effect of SFS concentration

To determine the minimum amount of reducing agent required for SFS-based PET decolorization, treatments using 5, 10, 15, 20, 25, 30, 35 and 40 g/L SFS were investigated. Table 14 summarizes the K/S values for the fabric samples, and Figures 38 and 39 capture these data in the form of a graph and a photograph, respectively.
Table 14 K/S value Vs SFS concentration for dark grey commercial PET fabric after treatment in water/acetone (1:2) at 110 °C for 30 min.

<table>
<thead>
<tr>
<th>[SFS] (g/L)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/S value</td>
<td>3.08</td>
<td>0.41</td>
<td>0.63</td>
<td>1.43</td>
<td>1.78</td>
<td>12.72</td>
<td>7.02</td>
<td>2.76</td>
</tr>
</tbody>
</table>

Figure 38 Graph of K/S value Vs SFS concentration for dark grey commercial PET fabric after treatment in water/acetone (1:2) at 110 °C for 30 min.
Figure 39 PET fabrics showing the effect of SFS concentration on decolorization of dark grey commercial sportswear in water/acetone (1:2) at 110 °C for 30 min.

By repeating the control experiment for SFS concentrations twice, the results obtained show an unexpected trend, which can be divided into three parts. Firstly, K/S value decreased when increasing SFS concentration from 5 to 10 g/L. Then it increased as the SFS concentration increased further, and reached a peak at 30 g/L. After that, K/S values dropped back to a low level again. In the beginning, more dye was reduced by adding more reducing agent. The reason why the second and third parts were produced is unclear, but it is believed that they are due to the conversion of initially uncolored products or intermediates to secondary colors followed by secondary color degradation.

A large excess of SFS (40g/L or more) does not improve dye degradation. Sufficient decolorization performance may be achieved with concentrations as low as 10 g/L.
4.2.2.4 The effect of temperature

Temperature is another very important parameter that will have a significant influence on decolorization. Experimental results regarding this series of experiments are presented in Table 15, Figures 40 and 41.

Table 15 K/S value Vs temperature for dark grey commercial PET fabric after SFS (10g/L) treatment in water/acetone (1:2) for 30 min.

<table>
<thead>
<tr>
<th>Temp. (˚C)</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/S value</td>
<td>95.02</td>
<td>19.88</td>
<td>2.39</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Figure 40 Graph of K/S value Vs temperature for dark grey commercial PET fabric after SFS (10g/L) treatment in water/acetone (1:2) for 30 min.
Figure 41 PET fabrics showing the effect of temperature on decolorization of dark grey commercial sportswear using SFS (10g/L) treatment in water/acetone (1:2) for 30 min.

A strong temperature dependence for the PET decolorization was observed. Even though 80 °C and 90 °C are higher than the Tg of PET (67~81°C), too little dye gets extracted and decolorized. Decolorization at 100 °C and 110 °C was much more effective. It is well known that, dyeing of polyester with disperse dyes is a completely different dye transfer system from dyeing of hydrophilic fibers. Disperse dye molecules can only penetrate the amorphous region, and the diffusion of dye molecules from the fibers surface into the body of polymer can only occur when temperature is above its Tg. Because at temperature below Tg, the polymer molecule chains do not have enough energy to allow them to move around. When enough heat is applied, polyester changes from rigid structure to a flexible structure, which is known as the rubbery state. Then the dye molecules can grasp the opportunity to slip between the movable segments into the interior of the fiber. By the same token, decolorization most efficiently takes place at such elevated temperature. The first step of decolorization is extraction, which involves dye transfer from solid fibers to the liquid medium. After dyes arrive in the medium,
they will be more readily reduced by SFS, thus driving more dye out from fiber. In polyester dyeing process, there is a dyeing transition temperature at which the rate of dye diffusion becomes very rapidly [21]. It cannot be just coincident with Tg, but usually much higher than it. This helps to explain the experimental results that higher bath temperature leads to better decolorization. For the purpose of cost effectiveness, 100 °C was deemed suitable for laboratory-scale experiments.

4.2.2.5 The effect of liquor ratio

Liquor ratio is an important parameter in batch dyeing, and is defined as the weight ratio between the total dry material and the bath volume. So, for example, a liquor ratio of 1:10 means 10 liters of bath per kilogram textile material. Experiments designed to investigate the effect of liquor ratio, were actually aimed to find the minimum liquor ratio needed. Results are demonstrated in Table 16, Figure 42 and Figure 43.

<table>
<thead>
<tr>
<th>Liquor ratio</th>
<th>K/S value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>29.33</td>
</tr>
<tr>
<td>1:20</td>
<td>14.44</td>
</tr>
<tr>
<td>1:30</td>
<td>5.98</td>
</tr>
<tr>
<td>1:40</td>
<td>5.04</td>
</tr>
<tr>
<td>1:50</td>
<td>2.39</td>
</tr>
</tbody>
</table>

Table 16 K/S value Vs liquor ratio for dark grey commercial PET fabric after SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.
Figure 42 Graph of K/S value Vs liquor ratio for dark grey commercial PET fabric after SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.

Figure 43 PET fabrics showing the effect of liquor ratio on decolorization of dark grey commercial sportswear using SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.
The results show that the K/S value decreased, with increasing liquor ratio. A small liquor ratio (1:10 or 1:20) was insufficient for decolorization, while 1:50 gave substantial color removal in the Ahiba lab dyeing machine. However, the liquor ratio differs greatly between machine types. Mechanical factors of wet processing equipment, such as bath and fabric turnover rate, turbulence and physical/flow characteristics could influence the liquor ratio significantly. Using low-liquor ratio equipment, the weight of bath used to dye and/or decolorize a give weight of goods can be reduced as a result.

4.2.3 Summary of the optimized method

The above experiments led to an optimized decolorization method using SFS. The optimized method is presented in

Table 17.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[SFS]</td>
<td>10g/L</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>110 °C</td>
<td></td>
</tr>
<tr>
<td>L.R.</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Water: Acetone</td>
<td>1:2</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>30 min</td>
<td></td>
</tr>
</tbody>
</table>

4.2.4 Decolorization using optimized method

To determine the scope of disperse dye structures that can be decolorized on PET, different classes of dyes were treated with SFS using the optimized method. The results are presented
in Table 18, where it is shown that the disperse dyes include two azo, two anthraquinone, and two nitro structures, while the basic dye used is a methine dye. These colorants may not be expected to have their chromophores reduced to the same extent, so the change of perceived color (difference between K/S values before and after treatment), along with Whiteness Index were used to characterize the decolorization performance. Figure 44 and Figure 45 give the visual assessments.

Table 18 Decolorization performance of optimized SFS method for different disperse dyes in cationic dyeable PET fabric.

<table>
<thead>
<tr>
<th>Samples</th>
<th>K/S values Before treatment</th>
<th>K/S values After treatment</th>
<th>Whiteness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse Orange 30, 1.0%owf</td>
<td>65.64</td>
<td>0.51</td>
<td>70.21</td>
</tr>
<tr>
<td>Disperse Blue 79, 1.0%owf</td>
<td>81.02</td>
<td>1.12</td>
<td>70.15</td>
</tr>
<tr>
<td>Disperse Yellow 42, 1.0%owf</td>
<td>16.80</td>
<td>0.22</td>
<td>78.26</td>
</tr>
<tr>
<td>Disperse Yellow 86, 1.0%owf</td>
<td>19.16</td>
<td>0.44</td>
<td>76.56</td>
</tr>
<tr>
<td>Disperse Red 60, 1.0%owf</td>
<td>48.33</td>
<td>0.24</td>
<td>75.60</td>
</tr>
<tr>
<td>Disperse Blue 56, 1.0%owf</td>
<td>103.94</td>
<td>1.27</td>
<td>69.66</td>
</tr>
<tr>
<td>Basic Yellow 28, 0.75%owf</td>
<td>33.93</td>
<td>1.77</td>
<td>70.34</td>
</tr>
</tbody>
</table>
Figure 44 Cationic dyeable PET fabrics dyed by disperse dyes (1.0% owf), before and after SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.

Figure 45 Cationic dyeable PET fabrics dyed by basic dye (0.75%), before and after SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.

All the fabrics became very white after SFS treatment, even the two blue samples. The efficacy of this optimized method for the dyes used has been confirmed by the low K/S values and acceptable Whiteness Indexes.
This method has other advantages. It is very easy, a one-step process, and only one chemical (sodium formaldehyde sulfoxylate) is needed. Secondly, the treatment temperature (100˚C) is relatively low, compared with standard dyeing process. In addition, this method is applicable to normal PET and cationic dyeable PET.

4.3 Bath reuse

Experiments involving reuse of water/acetone solvent media for 5 cycles were carried out using cationic dyeable PET dyed with Disperse Yellow 42 and Disperse Blue 56 at 1% on-weight-of-fiber. At the end of each cycle, fabric samples were squeezed thoroughly after being removed from the bath, to maximize the amount of solvent left in the bath. K/S and Whiteness Index values were determined and are reported in Table 19 (Yellow 42) and Table 20 (Blue 56).

Table 19 K/S and Whiteness Index values for Yellow 42 cationic dyeable PET after 5 uses of bath in SFS (10g/L) treatment in water/acetone (1:2) at 100 ºC for 30 min.

<table>
<thead>
<tr>
<th>Round Number</th>
<th>K/S value</th>
<th>Whiteness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.22</td>
<td>78.26</td>
</tr>
<tr>
<td>2</td>
<td>0.28</td>
<td>76.27</td>
</tr>
<tr>
<td>3</td>
<td>0.38</td>
<td>73.12</td>
</tr>
<tr>
<td>4</td>
<td>0.49</td>
<td>71.76</td>
</tr>
<tr>
<td>5</td>
<td>0.72</td>
<td>70.86</td>
</tr>
</tbody>
</table>

Since SFS, but not water/acetone, was consumed during the decolorization process, 10g/L SFS was added each time to reconstitute the bath. It can be seen from Table 19 that K/S values
increased, and Whiteness Index decreased as the cycles progressed, but the changes were small. Even after 5 uses of the same bath, fabrics obtained still appeared to be very white (Figure 46). It is probable that the solvent still possessed decolorization ability after five cycles.

Figure 46 Yellow 42 dyed Cationic dyeable PET fabric after 5 reuses of bath in SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.

The darkness of residual bath increased as well. The bath became so saturated that it even contaminated the beaker surface. It can be seen that the bath contained a dark colored precipitate at the bottom. Figure 47 shows copy of photograph of the residual bath at the end of the first and fifth rounds.

Figure 47 Final bath from SFS after decolorization of the 1st (left) and 5th Yellow 42 dyed cationic dyeable PET fabric (right)
Table 20 K/S and Whiteness Index values for Blue 56 dyed cationic dyeable PET fabric after 2 reuses of bath containing water/acetone (1:2) SFS (10g/L) treatment at 100 °C for 30 min.

<table>
<thead>
<tr>
<th>Round Number</th>
<th>K/S value</th>
<th>Whiteness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.27</td>
<td>69.66</td>
</tr>
<tr>
<td>2</td>
<td>6.88</td>
<td>58.31</td>
</tr>
</tbody>
</table>

Figure 48 Blue 56 dyed Cationic dyeable PET fabric after 2 reuses of SFS (10g/L) treatment in water/acetone (1:2) at 100 °C for 30 min.
Figure 49 Final bath from SFS decolorization of the 1st (left) and 2nd Blue 56 dyed cationic dyeable PET fabric (right)

Reusing water/acetone bath to decolorize Blue 56 achieved worse results than Yellow 42. After 2 uses of the same bath, fabric obtained became dark grey (Figure 48). The 1st bath from Yellow 42 decolorization was colorless, which indicated a complete decolorization of fabric and the absence of secondary colors, whereas the residual bath from Blue 56 was very dark. Therefore, the fabrics chosen for testing represented two extremes within our study.

4.4 Fabric strength assessments

To determine whether fiber degradation occurred when dye PET fabrics were subjected to SFS decolorization at elevated temperature, intrinsic viscosity was measured using an Ubbelohde viscometer and viscosity-average molecular weight was calculated by applying Mark-Houwink equation:

$$[\eta] = 3.72 \times 10^{-4} M^{0.73}$$

In this investigation, the control was untreated 100% PET warp knit fabric, while the variables were randomly selected decolorized PET fabrics which had been dyed by Disperse Orange 30 and Disperse Blue 60. Intrinsic viscosity and molecular weight of these three fabrics are recorded in Table 21.

Table 21 Intrinsic viscosity (IV) Vs Viscosity-average molecular weight for control PET fabric and PET fabric after SFS (40g/L) treatment in acetone/water (1:1) at 100 °C.

<table>
<thead>
<tr>
<th>Fabric</th>
<th>IV (dL/g)</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.5024</td>
<td>19425</td>
</tr>
<tr>
<td>Decolorized Orange 30</td>
<td>0.4999</td>
<td>19302</td>
</tr>
<tr>
<td>Decolorized Blue 60</td>
<td>0.5002</td>
<td>19349</td>
</tr>
</tbody>
</table>
It was found that the intrinsic viscosity and viscosity-average molecular weight essentially remained the same. Polymer fibers present a wide range of mechanical properties depending on their molecular weight. Polyester with a MW of ~15,000-20,000 is used for oriented films and textile fibers [61]. Higher levels of polymerization, which means higher molecular weight, produces higher strength fibers. Although this technique does not provide us any information on the shapes of the molecular weight distribution, it gives us a general idea that degradation of PET fiber did not occur during treatment.
Chapter 5 Conclusion

Sodium formaldehyde sulfoxylate (SFS) can be used to decolorize disperse dyes in water/acetone media. After demonstrating the potential of this method, studies towards optimization of the process on dyed PET gave the following:

1) While a longer treatment time of 60 min gives better decolorization, a processing time of 30 min is sufficient.

2) A water to acetone ratio of 1:2 gives the best decolorization performance. Too much water or too much acetone reduces the decolorization effectiveness.

3) Sufficient decolorization performance can be achieved with an SFS concentration as low as 10 g/L.

4) There is a strong temperature dependence for decolorizing polyesters. For the purpose of cost effectivity, 100 °C is deemed suitable.

5) On a laboratory scale, the best liquor ratio is 1:50, which gives substantial color removal.

The SFS decolorization method was applied to various PET fabric samples containing dyes with different chromophores. Among them quinoline dye was very difficult to decolorize, whereas azo, nitro, anthraquinone and methine dyes were decolorized thoroughly.

In addition, experiments involving reuse of water/acetone medium were carried out on Disperse Yellow 42 and Disperse Blue 56. For Yellow 42, the bath could be reused for five times and there was a possibility that the solvent still possessed decolorization ability. While for Blue 56, full decolorization could not be achieved when the bath was reused for the second time.
Meanwhile, degree of polymerization of decolorized samples were measured to determine whether fiber degradation occurs. From the results, it is clear that SFS decolorization has no significant influence on the mechanical properties of PET fabrics.
Chapter 6 Future Work

The following areas are recommended for future work.

(1) Investigation of the sodium formaldehyde sulfoxylate (SFS) reduction mechanism for various dyes

(2) Analysis of precipitate and other products in aqueous solution

After decolorization, there were precipitates in the solutions. In some occasions, the decolorized solution possessed colors which differed from the original color of samples. It is believed to be related with the reduction of chromophores. The investigation of reduction mechanism can help to characterize the products after reactions. TLC, HPLC-MS and NMR will be used to characterize the compounds left in the solutions. In addition, TEM and EDS will be used to identify the precipitates in the solution and even on the surface of fabric.

(3) Detection and prevention of hazardous emissions

SFS contains sulfur atoms in its structure, which are very likely to produce hydrogen sulfide (H$_2$S), sulfur dioxide (SO$_2$) and other sulfur-containing hazardous gases. It is also known that the decomposition of SFS at high temperature leads to the generation of formaldehyde (CH$_2$O). GC-MS can be used to detect different gases that may accompany decolorization. Preventions, for example, absorption steps should be carried out if there are indeed hazardous emissions.

(3) Scaling up from laboratory to pilot plant

Before scaling up to the ultimate commercial practice, pilot plant can be of immense use. The lab-scale experiment can then be studied in a representative model of the large-scale production plant. Pilot plant will help to facilitate the small scale research to a full scale production faster
and with less risk. It will also help to put the economics and environment impacts in focus and assess the marketability of this method.

(4) Life Cycle Assessment.

Life Cycle Assessment (LCA) should be carried out, regarding PET fabrics produced by virgin polyesters and recycled polyester fabrics decolorized by SFS reduction procedure. It is a systems-based approach to quantifying the human health and environmental impacts associated with the PET garment’s life from “cradle to grave.” The most important goal of LCA is to minimize the magnitude of pollution [62].
Chapter 7 References


40. Mueller, B., Neubueser, I., & Gross, W. Agent, useful in the decolorization of substrates with dyes e.g. polyester, polyamide, cotton and hairs, comprises sulfinic acid derivative in a carrier and a non-ionic surfactant. 2006.

41. Wasinger, E. M. Composition for desizing and decolourising fabric/garment, e.g. denim - includes around 40 to 60% by weight of reducing agent selected from group. US725630 03 Oct 1996.


60. AATCC Test Method 110, American Association of Textile Chemists and Colorists Technical Manual, 2009


APPENDICES
Appendix A

Figure 50 Ahiba Spectradye Plus dyeing machine.

Figure 51 Spectraflash SF 600X Datacolor Reflectance Spectrophotometer.
Figure 52 HP/Agilent 8453 UV-Vis Spectrophotometer.