

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**OPTIMIZATION OF REACTIVE DYEING OF COTTON FIBER WITH  
REAL-TIME MONITORING SYSTEM**

**Ph.D. THESIS**

**Mehmet ÖZTÜRK**

**Department of Textile Engineering**

**Textile Engineering Programme**

**DECEMBER 2011**



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**DECEMBER 2011**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**GERÇEK ZAMANLI İZLEME SİSTEMİ İLE PAMUK LİFİNİN REAKTİF  
BOYALAR İLE BOYANMASININ OPTİMİZASYONU**

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*To Fatoş,*



## **FOREWORD**

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## ABBREVIATIONS

|                                    |  |
|------------------------------------|--|
| <b>a*</b>                          | : Red/Green Value                        |
| <b>b*</b>                          | : Yellow/Blue Value                      |
| <b>B</b>                           | : Bridge Group                           |
| <b>C</b>                           | : Chromophore                            |
| <b>Cell-OH</b>                     | : Cellulose Anion                        |
| <b>C.I.</b>                        | : Colour Index                           |
| <b>D</b>                           | : Dye                                    |
| <b>DOA</b>                         | : Alcoholysis of Dye                     |
| <b>DOH</b>                         | : Alcoholysis of Dye                     |
| <b>FIA</b>                         | : Flow Injection Analysis                |
| <b>HPLC</b>                        | : High Performance Liquid Chromatography |
| <b>K/S</b>                         | : Color Strenght                         |
| <b>L*</b>                          | : Lightness Value                        |
| <b>L:R</b>                         | : Liquor Ratio                           |
| <b>o.w.f.</b>                      | : On Weight of Fabric                    |
| <b>R</b>                           | : Reactive System                        |
| <b>SIA</b>                         | : Sequential Injection Analysis          |
| <b>UV</b>                          | : Ultra Violet                           |
| <b>W</b>                           | : Water Solubilizing Group               |
| <b><math>\lambda_{\max}</math></b> | : Wavelenght of Maximum Absorption       |





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## **OPTIMIZATION OF REACTIVE DYEING OF COTTON FIBER WITH REAL-TIME MONITORING SYSTEM**

### **SUMMARY**

The increased public awareness and concerns about the environmental impact of the coloration industry, the increased cost of energy, labor, water and auxiliaries as well as the associated costs of processing colored effluents require the optimization and control of all factors influencing the uptake of dye by fiber, including the liquor to goods ratio, temperature, electrolyte concentration, pH, as well as the type of dyes employed. These are the most well established influential factors affecting the depth of shade of dyed goods as well as the uniformity of the coloration process.

Dyebath monitoring technologies have been used to control over the dyeing process. Using these technologies can result in optimized dyeing process, improved product quality, detection of errors and reduced environmental impact. The economical advantages of the optimized dyeing processes are significant in today's competitive textile markets. To effect a high level of control the dyeing process, the profile of the exhaustion curves of each dye in the dye mixture recipe is the most essential information. This can be used for the evaluation of several important factors in order to optimize the dyeing processes. The compatibility of dyes is another significant factor which can be tested by this method. Despite lots of studies conducted over the last several decades to demonstrate the role of individual dyeing parameters on the outcome of dyeing, it has only recently become possible to investigate the exhaustion profile of individual dyes in an admixture in real-time.

In this study, a real-time monitoring device was used to investigate the reactive dyeing of cotton with a commercial trichromatic dye formulation at different dyeing parameters. The effect of variation in these parameters on individual exhaustion profiles and fixation properties of each dye was examined. Color fastness properties of dyed fabrics were also investigated. A central composite design was used to optimize the dyeing parameters. In addition, the compatibility of dyes in the dyeing recipe was evaluated. It was shown that a change in the parameters affects the exhaustion and fixation rate of each dye differently resulting in a significant change in the depth of shade as well as the final hue of the colored product. The results of this study can help dyers to obtain a more appropriate selection of dyes for recipes requiring several dyes and reduce the need for stripping or re-dyeing of colored goods.



## **GERÇEK ZAMANLI İZLEME SİSTEMİ İLE PAMUK LİFİNİN REAKTİF BOYALAR İLE BOYANMASININ OPTİMİZASYONU**

### **ÖZET**

Boyama endüstrisinin çevresel etkileri hakkındaki artan bilinçlenme ve endişeler, artan enerji, işçilik, su ve yardımcı kimyasal maliyetlerinin yanı sıra renklenmiş atık suların işlenmesi ile ilgili maliyetler, boyanın life alınımını etkileyen tüm faktörlerin (flotte oranı, sıcaklık, tuz konsantrasyonu, pH ve uygulanan boyanın tipi) optimizasyonunu ve kontrolünü gerekli kılmaktadır. Bunlar, boyanmış ürünün rengini ve düzgün bir renklendirme işlemi yapılmasını etkileyen en önemli faktörlerdir.

Boya banyosunu izleme teknolojileri, boyama işlemini kontrol etmek için kullanılmaktadır. Bu teknolojilerin kullanımı, boyama işleminin optimize edilmesini, daha iyi ürün kalitesini, hataların belirlenmesini ve çevreye verilen zararın azatılmasını sağlar. Optimize edilmiş boyama işlemlerinin kullanılmasının getirdiği ekonomik avantajlar, günümüzün rekabetçi piyasa koşulları açısından oldukça önemli hale gelmiştir. Boyama işlemini en iyi şekilde kontrol etmek için, boya reçetesindeki her bir boyanın boya alma eğrisi çok önemli bir bilgidir. Bu bilgi, boyama işlemlerini optimize etmek için bir çok önemli faktörün değerlendirilmesinde kullanılabilir. Önemli bir parametre olan boyaların birbirleri ile olan uyumu da bu metod ile test edilebilir. Her bir boyama parametresinin boyamadaki rolünü izah etmek için birçok çalışma yapılmasına rağmen, karışım reçetesindeki her bir boyanın gerçek zamanlı boya alma profilini araştırmak son yıllarda olası hale gelmiştir.

Bu çalışmada, pamuklu kumaşın ticari bir trikromatik (üç renkli) reaktif boya reçetesi kullanılarak ve boyama parametreleri değiştirilerek boyanmasını incelemek için gerçek zamanlı izleme cihazı kullanılmıştır. Bu parametrelerdeki değişimlerin her bir boyanın boya alma ve fikse olma özelliklerine olan etkisi araştırılmıştır. Boyama parametrelerini optimize etmek ve yeni bir boya reçetesi oluşturmak için, deneysel tasarım metodu kullanılmıştır.

Çalışmanın ilk aşamalarında, deneysel tasarım metodunda kullanılan parametrelerin temel seviyelerini belirlemek için ön denemeler yapılmıştır. Boyama sıcaklığının ve alkali ekleme yönteminin boyama üzerine olan etkisi incelenmiştir. Kullanılan üç farklı sıcaklığın içinde en uygun olanı belirlenmiştir. Alkalinin tamamının aynı anda eklenmesi yerine porsiyonlar halinde ve fikse olma sıcaklığına ulaştıktan sonra eklenmesinin ve daha avantajlı olduğu bulunmuştur.

Boyama sıcaklığı artış hızının etkisini araştırmak için iki farklı sıcaklık artış hızı kullanılarak ön denemeler yapılmıştır. Bu iki sıcaklık artış hızının boyama üzerine olan etkileri arasında belirgin bir fark bulunamadığı için daha yüksek olan tercih edilmiştir, çünkü daha yüksek artış hızını kullanmak boyama süresini azalttığı için daha avantajlıdır.

Daha önce yapılan ön denemelerde boyama işlemi herhangi bir soğutma işlemi olmadan sonlandırılmıştır. Boyama işleminin sonundaki soğutma aşamasının boyama performansı üzerine pozitif etkisi olduğu bulunmuştur.

Yapılan ön denemelerin sonuçlarına göre boyama prosedüsü modifiye edilmiştir. Modifiye edilen prosedürde, alkali ve tuz miktarından bağımsız olarak, alkalinin ilk porsiyonu sıcaklık artışı aşamasının ortasında, geriye kalan iki porsiyon sıcaklık artışı tamamlandığında eklenmiştir. Ayrıca modifiye edilen prosedürde boyamanın sonunda soğutma aşaması ilave edilmiştir.

Modifiye edilen yeni prosedür kullanılarak, alkali ve tuz miktarının boyama üzerine olan etkisini incelemek için ön denemeler yapılmıştır. Bu ön denemelerde boya banyosuna alkali ve tuz ilave edilmediğinde kumaş üzerine herhangi bir boya alınmadığı, dolayısıyla da herhangi bir fikse olmadığı gözlenmiştir. Boya banyosuna sadece tuz veya sadece alkali eklendiğinde boya alma miktarı belirli bir seviyede kalmıştır. Boya banyosunda sadece tuz olduğunda elde edilen boya alma yüzdeleri sadece alkali olduğunda elde edilenlere göre daha yüksektir, diğer taraftan sadece alkali olduğunda elde edilen fikse olma yüzdeleri sadece tuz olduğunda elde edilene göre daha yüksektir. Ön denemelerin bu bölümünde aşırı düşük ve aşırı yüksek miktarda tuz ve alkali kullanmanın etkileri de incelenmiş ve yüksek miktarda tuz ve alkali kullanılmasının boyamayı negatif olarak etkilediği bulunmuştur. Böylece tuz ve alkalinin tekil ve birlikte olan etkileri belirgin bir şekilde açıklanmıştır.

Flotte oranının boyama üzerine olan etkisini incelemek için, beş farklı flotte oranı kullanılarak ön denemeler yapılmıştır. Flotte oranı azaldıkça boya alma yüzdesinin arttığı bulunmuştur. Ancak çok düşük flotte oranlarında boyama yapıldığında da boyama düzgünsüzlüğü artmaktadır. Bu nedenle optimum bir flotte oranı seçilmesi gerekmektedir.

Boyama işleminin en önemli amaçlarından biri istenilen doğru renk tonunu elde etmektir. Bu durum genellikle, kırmızı mavi ve sarı renkteki boyaların karışımının kullanılmasını gerektirir. Yapılan ön denemeler esnasında, kullanılan boya reçetesi ticari bir reçete olmasına rağmen, karışımda kullanılan boyaların birbirleri ile uyumlu olmadığı görülmüştür. Boya alma eğrileri, bir boyanın boyama özelliklerini karakterize etmek ve birbirleri ile uyumlu boyaları seçmek için kullanılabilir. Genellikle boyaların uyumluluğunu belirlemek için boya karışımındaki her bir boya tek tek kullanılarak aynı koşullar altında çeşitli boyamalar yapılır. Benzer boya alma hızlarına sahip boyaların aynı karışım içinde kullanılırsa uyumlu olacağı düşünülmektedir. Ancak boyalar birlikte kullanıldığında ortaya çıkan durum bilinmemektedir. Bu çalışmada kullanılan izleme sistemi ile karışımda kullanılan kırmızı boyanın diğer iki boya ile uyumlu olmadığı tespit edilmiştir. Kırmızı boya tek başına kullanıldığında yüksek boya alma seviyesine ulaşılmıştır. Ancak kırmızı boya diğer iki boyadan biriyle birlikte kullanıldığında kırmızı boyanın boya alma seviyesi düşmektedir. Kırmızı boyanın diğer boyalar ile rekabet edemediği düşünülmektedir. Bu nedenle yeni bir kırmızı boya kullanılmasına karar verilmiştir, fakat boyama reçetesindeki kırmızı boya değiştirildiğinde kumaşın renk tonu da değişecektir. Bu durumu önlemek için yeni kullanılan kırmızı boyanın miktarı ayarlanmıştır. Yeni kullanılan kırmızı boya ile her üç boya için de yüksek boya alma seviyelerine ulaşılmıştır ve kumaşın renk tonundaki değişim istenilen toleranslar içinde kalmıştır.

Boyanmış kumaşların renk haslığı özellikleri de incelenmiştir. Reaktif boyaların yüksek renk haslığı özelliklerine sahip olmaları nedeniyle boyama parametrelerindeki değişimlerin boyama performansı üzerine belirgin bir etkisi görülmemiştir.



Çalışmanın son bölümünde deneysel tasarım metodu kullanılarak boyama işlemi optimize edilmiştir. İki farklı boya reçetesi için tuz ve alkali miktarları, boyama sıcaklığının ve fıkse olma aşamasındaki bekleme zamanının optimum seviyeleri belirlenmiştir. Elde edilen optimum reçeteler kullanılarak yapılan boyamaların sonuçları ile tahmin edilen sonuçlar birbirine yakın çıkmıştır. Bu çalışmanın sonuçlarının, birçok boya içeren reçeteler için daha uygun boyaların seçimini sağlamaya ve renklendirilmiş ürünün boyasının sökülmesi veya tekrar boyanması gibi ihtiyaçların azaltmasına yardımcı olacağı düşünülmektedir.



## **1. INTRODUCTION**

### **1.1 Introduction and Aim of the Study**

Real time dyebath monitoring and control devices have been proposed and employed over the last two decades to improve the efficiency of dyeing process and reduce associated operation and overall costs. While fiber reactive dyes are currently considered to be a common class of dye applied to cellulosic fibers, their introduction and subsequent application has resulted in a significant step forward in improving the overall performance of dyed cellulosic fibers. This is due to their excellent wet fastness properties, exceptional brightness, wide range of available colors and relatively simple application methods. Because of these attractive features, the demand for fiber reactive dyes has increased over the last several decades [1] and they enjoy a comfortable share of the market and remain amongst the most important category of dyes applied to cellulosic fibers. However, in the reactive dyeing of cotton, a range of variables contribute to final exhaustion and fixation of dye onto the substrate which include the liquor to goods ratio, temperature, electrolyte concentration, pH, as well as the type of dyes employed [2,3].

In this study, a real time dyebath monitoring system was employed to explore the effect of variations in dyeing parameters on exhaustion and fixation profiles of individual dyes in dyeing of cellulosic fibers using a trichromatic fiber reactive recipe. We followed a designed experiment containing electrolyte concentration, alkali concentration, temperature and time and optimized the reactive dyeing in terms of exhaustion and fixation results.



## 2. LITERATURE REVIEW

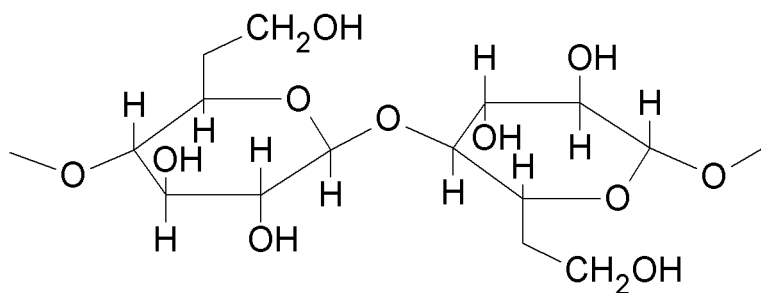
### 2.1 Cellulosic Fibers

Cellulose is the most plentiful organic polymer, which occurs naturally. Cotton is the most important natural textile fiber as well as cellulosic textile fiber. Cotton comes from the seed hair of plant in the Gossypium family [4]. Viscose rayon, cupraammonium rayon, linen and jute are other natural and manufactured cellulosic fibers that can be dyed with the same dyes applied on cotton [5].

Cotton fibers have a fibrillar structure. The outermost layer of the fiber is the cuticle, which is relatively hydrophobic because of the waxes and fats. This layer has to be removed to render the fibers more water absorbent [6]. Beneath the cuticle is the primary wall of the fiber cell composed of a network of cellulose fibrils. The secondary wall consists of the bulk of the fiber. It is build up of sequential layers of the fibrils arranged spirally around the fiber axis. The spiral angle of the fibril varies one layer to the next. The lumen is a hollow canal in the center of the fiber [5-7].

#### 2.1.1 Molecular structure of cellulose

Cellulose is a 1-4 linked linear polymer of  $\beta$ -D-glucopyranose and shown in Figure 2.1. Glucose is the monomer unit of the cellulose polymer. These monomers are joined together by the loss of a molecule of water between the terminal hydroxyl groups attached to number 1 carbon atom of one glucose molecule and the number 4 carbon atom of another [4].



**Figure 2.1 :** Chemical structure of cellulose [6].

Cellulose is a polyalcohol, and each glucopyranose ring in the chain comprises three hydroxyl groups. Each of glucose unit is rotated  $180^\circ$  around the molecular axis. This gives a linear polymer chain that is almost flat. This structure allows the close approach of neighbouring cellulose molecules necessary for the development of crystalline regions. The intermolecular hydrogen bonds between hydroxyl groups hold together the cellulose molecules. Cellulose does not dissolve in water, because the water does not penetrate into the compact crystalline regions. However, cotton is relatively hydrophilic. Because its porous structure allows penetration of water molecules between fibrils and into the amorphous regions with free cellulose hydroxyl groups [4,8].

The degree of polymerization of cellulose is related with its source. For natural cellulose, it can be as high as 14000, but purification involving treatment with alkali usually reduces to about 1000-2000 [5].

### **2.1.2 Chemical reactions of cellulose**

The chemical reactivity of cellulose is governed by the presence of hydroxyl groups and the supermolecular structure. The chemical reaction takes place in the accessible interfibrillar and amorphous regions of the fibers. There are two major reactions for cellulose: esterification and etherification. Cellulose is esterified mostly under acidic conditions. These reactions involve acetylation, nitration, phosphorylation and sulphation [4, 5]. The mineral acids catalyse hydrolysis of the bonds between the glucose unit and cause depolymerization eventually leading to the monomer, glucose [6]. Etherification is carried out in the presence of alkali. The important utilization of etherification of is in coloration of cotton with reactive dyes. An alkaline media transforms the cellulose to the cellulosate anion, which reacts with suitable reactive dyes by nucleophilic substitution or addition to form covalent bonds [4,9].

## **2.2 Reactive Dyes**

Reactive dyes are the most commonly used class of dye for dyeing of cotton fabrics. Under alkaline conditions, these dyes react with the ionized hydroxyl groups in cotton cellulose forming a covalent bond with the fiber. The strong bond between the reactive dye and the cellulose ensures good fastness to washing and the simple

chemical structures of the dyes often result in bright colors [6]. The other advantages of reactive dyes can be listed:

- Good levelness and reproducibility properties because of their reactivities,
- High affinity for cellulose,
- Stability of the dye-fiber bond is good,
- Simple dyeing procedures.

Due to the excellent characteristics of reactive dyes, there has been an inclination for these dyes. However, under the alkaline conditions necessary for the dye-fiber reaction, in addition to reacting with cellulose, they also react with water forming hydrolyzed dye. This hydrolyzed dye is incapable of reaction with the fiber. The other drawbacks of reactive dyes include [10]:

- Requirement of large amount of electrolyte and alkali,
- Much water, energy and long time required for wash-off procedures,
- Low exhaustion and fixation properties for some dyes,
- Most of them have poor in chlorine fastness.

### **2.2.1 History of reactive dyes**

The idea of immobilizing a dye molecule by covalent bond formation with reactive groups in a fiber originated in the early 1900s. Various chemical were found that reacted with the hydroxyl groups of cellulose and eventually converted into colored cellulose derivatives. The rather forcefull reaction conditions for this led to the false conclusion that cellulose was a relatively unreactive polymer. Possibly, because of this, a number of dyes now known to be capable of covalent bond formation with groups in wool and cotton were not initially considered as fiber-reactive dyes, despite the good fastness to washing of their dyeing [6,11].

In 1955, Rattee and Stephen established that dyeing cotton with water-soluble dyes containing dichlorotriazine groups from a neutral dyebath, followed by an increase of the pH value, resulted in a reactive chlorine atom on the triazine ring being substituted by an oxygen atom from a cellulose hydroxyl group. This lead to the introduction of the reactive dyes for cellulose by ICI in 1956 [12]. CIBA and ICI

both introduced reactive dyes with monochlorotriazine groups in 1957, and, in 1958, Hoechst introduced reactive dyes containing potential vinylsulfone groups [13].

In the subsequent years, various dyestuff manufacturers introduced a large number of reactive groups. The historical development of commercial reactive dyes is shown in Table 2.1 [14].

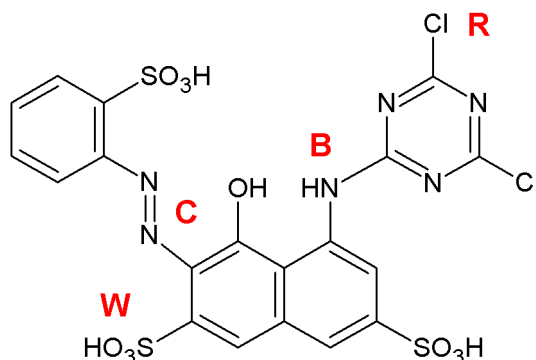
**Table 2.1 :** Summary of history of reactive dyes.

| <b>Commercial Name</b> | <b>Company</b> | <b>Year</b> |
|------------------------|----------------|-------------|
| Procion M              | ICI            | 1956        |
| Procion H              | ICI            | 1957        |
| Cibacron               | Ciba           | 1957        |
| Remazol                | Hoechst        | 1958        |
| Levafix                | Bayer          | 1958        |
| Reacton                | Geigy          | 1959        |
| Drimaren               | Sandoz         | 1959        |
| Levafix E              | Bayer          | 1961        |
| Elisiane               | Francolor      | 1963        |
| Primazin               | BASF           | 1964        |
| Solidazol              | Cassella       | 1964        |
| Procilan               | ICI            | 1964        |
| Levafix P              | Bayer          | 1966        |
| Lanasol                | CIBA           | 1966        |
| Reactofil              | Geigy          | 1968        |
| Verofix                | Bayer          | 1970        |
| Drimalan               | Sandoz         | 1970        |
| Procion HE             | ICI            | 1970        |
| Procion T              | ICI            | 1977        |
| Procion H – EG         | ICI            | 1979        |
| Kayacelon              | Nippon Kayaku  | 1984        |
| Procilene              | ICI            | 1987        |
| Cibacron C             | CIBA           | 1988        |

The characteristic features of a typical reactive dye molecule (see Figure 2.2) are the chromophore (C) with water solubilizing groups (W), the bridge group (B) and the reactive system (R). The chromophoric group contributes the color and substantivity



for cellulose. The reactive system enables the dye to react with the hydroxyl groups in cellulose. The bridging group attaches the reactive system to the chromophore. One or more solubilizing groups usually sulphonic acid substituents linked to the chromophoric groups [5].

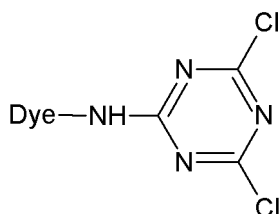


**Figure 2.2 :** Molecular structure of CI Reactive Red 1.

### 2.2.2 Reactive systems

The reactive systems of the various types of reactive dye have different chemical structures and show a wide range of reactivities.

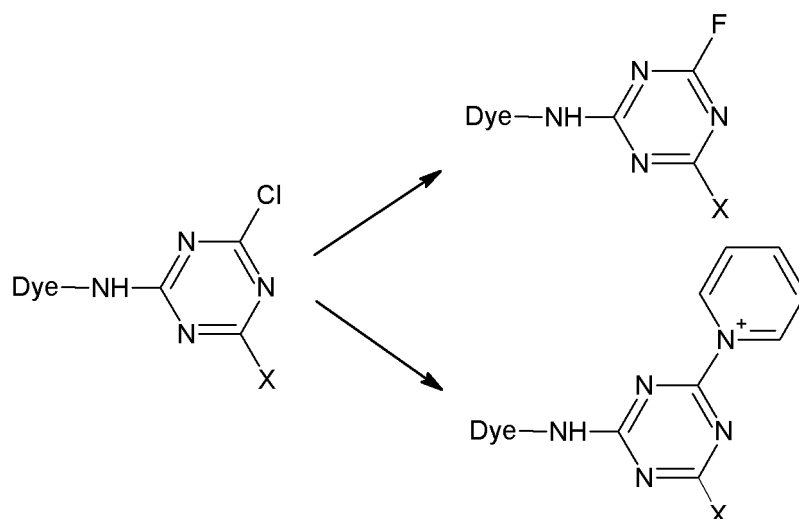
Most of the monoreactive dyes are derivatives of cyanuric chloride, a molecule of wide synthetic potential due to the different reactivities of the three chlorine atoms on the triazine ring. Careful selection of reaction conditions supplies a wide variety of triazine dyes. The highly reactive dichloroazine dyes are produced by condensation reaction of cyanuric chloride with a chromophore containing an amino group. These reactive dyes are sensitive to hydrolysis [15]. A typical structure of the dichlorotriazine dye is shown in Figure 2.3.



**Figure 2.3 :** Generic structure of the dichlorotriazine dye.

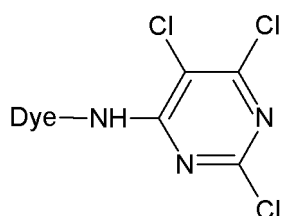
When a dichlorotriazine dye reacts with an amine at 25-40°C, a monochlorotriazine dye is generated. More aggressive reaction conditions, like high temperature and more alkali for batchwise application, are necessary for efficient fixation on cellulosic fibers [5, 16]. Replacing chlorine with fluorine can increase the reactivity of monochlorotriazine dyes, so the exhaust process is carried out at 40°C. In

addition, the highly reactive dyes can be produced by the reaction of monochlorotriazine dyes with tertiary amines (see Figure 2.4) [15].



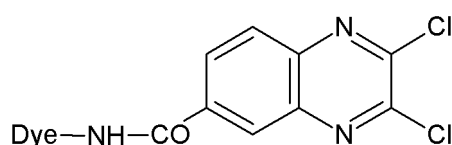
**Figure 2.4 :** Modifications of monochlorotriazine dye for generating fluoro and ammonium counterparts.

Other classes of heterocycles are important for the dyeing of cotton, especially halopyrimidine dyes. These dyes are less reactive than triazine dyes because of the diazine grouping in the pyrimidine ring, but dye-fiber bond of these dyes is more stable than those containing a triazine ring [5,15]. A typical structure of the halopyrimidine dye is shown in Figure 2.5.



**Figure 2.5 :** Generic structure of the halopyrimidine dye [6].

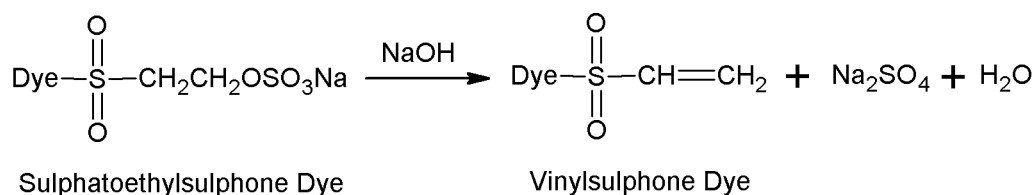
The reactivity of dichloroquinoxaline dyes (see Figure 2.6) corresponds roughly to those of dichlorotriazine dyes [15].



**Figure 2.6 :** Generic structure of the dichloroquinoxaline dye.

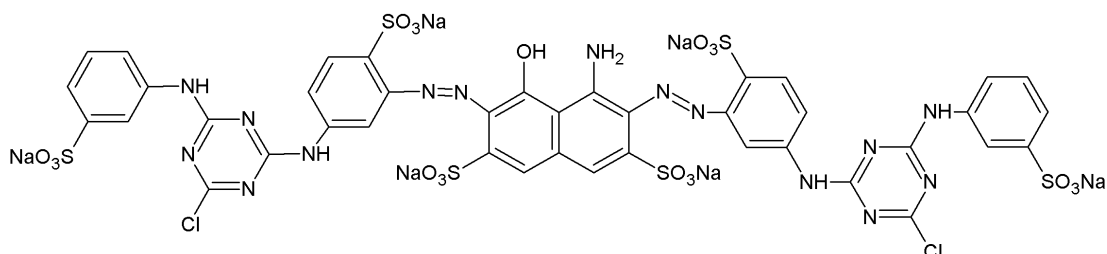
The vinylsulphone dyes containing the characteristic 2-sulphatoethylsulphonyl grouping have had the greatest effect on the dyeing industry [16]. Treatment with

alkali causes the abstraction of sulphuric acid to form a vinylsulfonyl moiety that reacts with cotton to give a dye-fiber bond (see Figure 2.7) [15].



**Figure 2.7 :** Conversion of sulphatoethylsulphone dye to vinylsulphone dye [5].

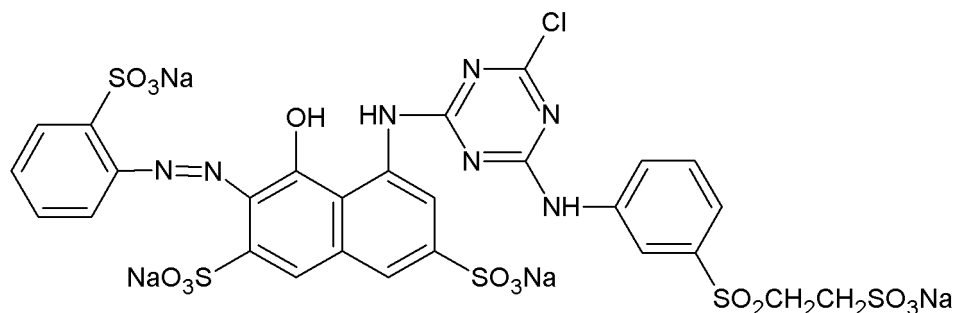
Bifunctional reactive systems have two separate reactive groups for reaction with suitable groups in the cotton. The aim was to produce bifunctional reactive dyes for exhaust dyeing that showed substantially higher substantivity, exhaustion and fixation values compared with corresponding monofunctional reactive dyes [5]. Bifunctional reactive dyes can be divided into two categories: homobifunctional dyes containing two of the same reactive groups and heterobifunctional dyes with two different reactive groups. The first category has structures in which two monochlorotriazine units are bonded with a suitable bridging group. Combining two different chromophores in a single system opens the way to certain color shades which are not easily possible via a single chromophore [15]. An example of the homofunctional reactive dye is shown in Figure 2.8.



**Figure 2.8 :** Chemical structure of CI Reactive Red 171 [15].

Heterobifunctional reactive dyes are characterized by two reactive groups with differing reactivities: a more reactive 2-sulphatoethylsulphone group and a less reactive monochlorotriazine unit. The presence of two different reactive groups supplies less sensitivity to dyeing temperature. They can be applied over a wide range of temperature (50-80°C) and reproducibility of hue in mixture recipes is improved. Vinylsulphone group gives reaction at low dyeing temperatures and the contribution of monochlorotriazine group to fixation becomes more valuable at higher temperatures [5]. An example of the homofunctional reactive dye is given in Figure 2.9.

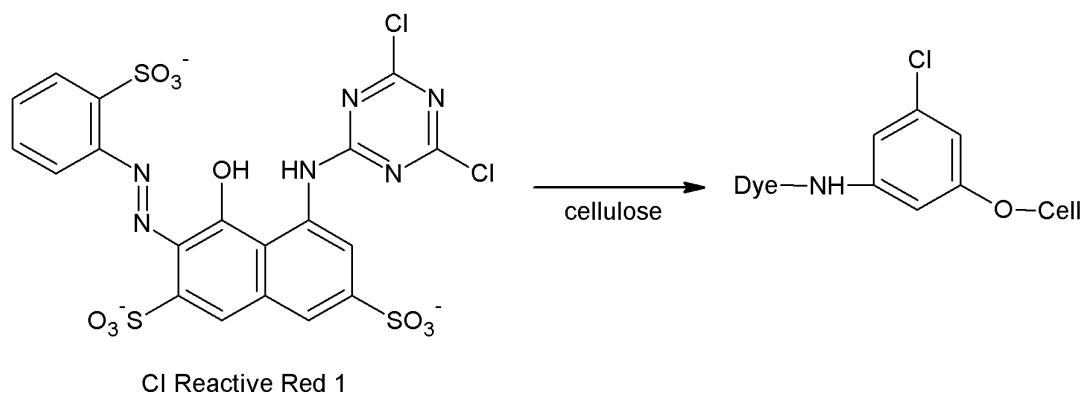
The incorporating of more than two reactive groups into the dye molecule has a minor effect on fixation properties. On the other hand, some important physical properties such as solubility, aggregation, substantivity and migration can be affected by these additional reactive groups.



**Figure 2.9 :** Chemical structure of CI Reactive Red 194 [5].

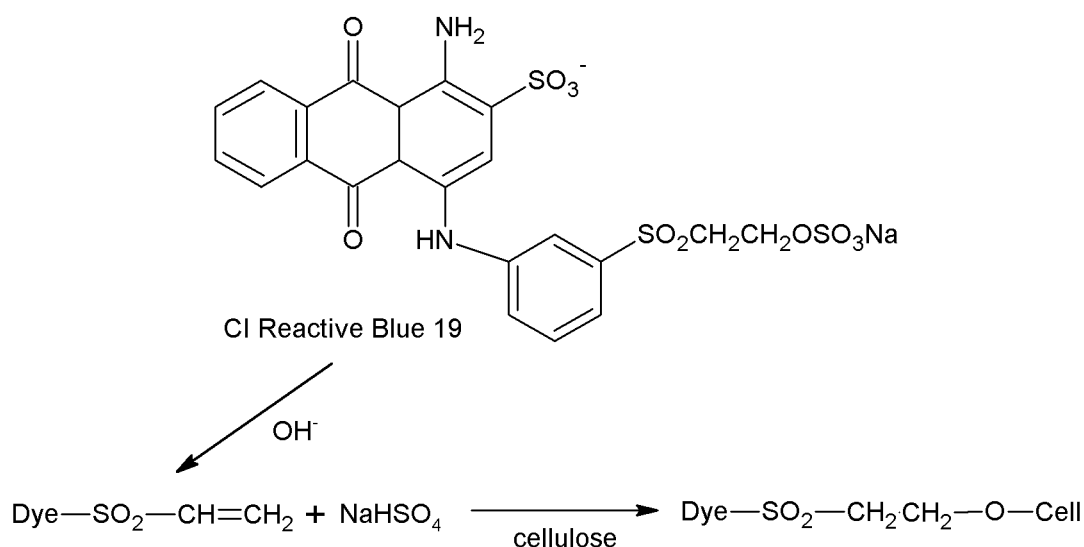
### 2.2.3 Dyeing reactions between reactive dye and cellulose

There are two types of chemical reaction between dye and cellulose: nucleophilic substitution and addition. In the nucleophilic substitution mechanism, a reactive dye reacts with cellulose by replacement of a chlorine, fluorine, methylsulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a heterocyclic ring [5,6]. The reaction of a dichlorotriazine dye with cellulose is typical of this process (see Figure 2.10).



**Figure 2.10 :** Nucleophilic substitution reaction of a reactive dye with cellulose [6].

In the nucleophilic addition mechanism, a nucleophilic group in the cellulose adds to a carbon-carbon double bond, usually activated by an adjacent electron-attracting sulphone group. Conversion of 2-sulphatoethylsulphonyl precursor group to vinylsulphonyl group is necessary in alkaline dyebath [5,6]. An example of this type of reaction is given in Figure 2.11.

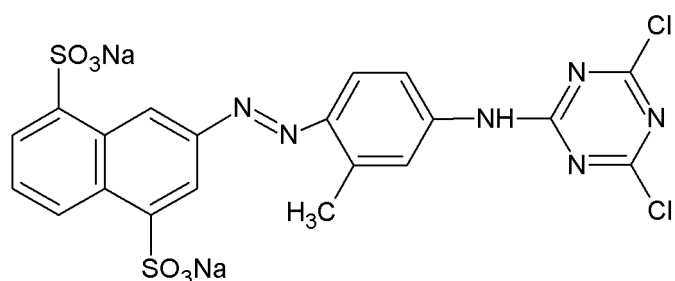


**Figure 2.11 :** Nucleophilic addition reaction of a reactive dye with cellulose [6].

#### 2.2.4 Chromophoric groups

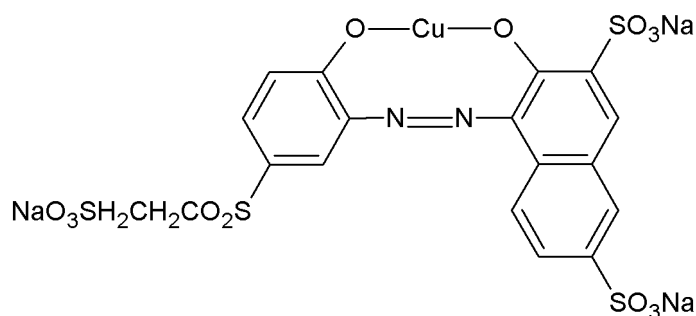
Chromophores give color to textile fibers. Different types of chromophoric group have been used in the production of reactive dyes including monoazo and disazo classes, metal complexes of azo dyes, formazan dyes, anthraquinones, triphenyldioxazines and phthalocyanines [5,17].

Most of the reactive dyes are based on azo dyes. Every hue in the color spectrum can be generated by appropriate structural modifications including mono and disazo dyes and combinations of single or multiple aromatic and heterocyclic systems [15]. While reddish yellows are generally obtained by arylazoanilines with the reactive group on the aniline ring, greenish yellow reactive dyes are monoazo derivatives with a heterocyclic coupling component and the reactive group located in the disazo compound [5]. An example of reactive dye with azo group is shown in Figure 2.12.



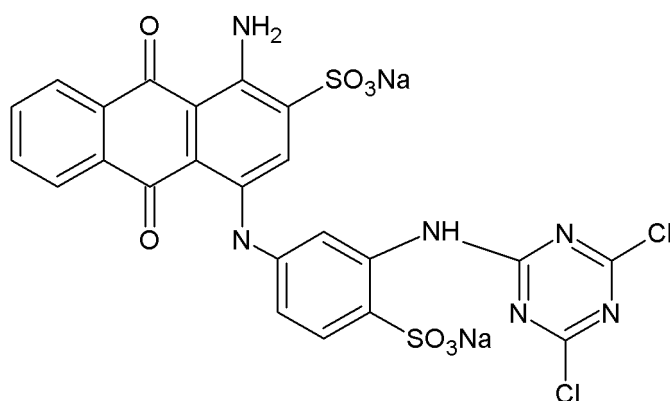
**Figure 2.12 :** Chemical structure of CI Reactive Yellow 4 [15].

Metal complex azo dyes have excellent light fastness properties. A wide range of colors can be obtained from copper complexes of azo components. CI Reactive Red 23 can be given as an example of metal complex azo dyes (see Figure 2.13) [15].



**Figure 2.13 :** Chemical structure of CI Reactive Red 23.

Due to their good light fastness, brilliance and chromophore stability over a wide pH range, anthraquinone reactive dyes are important. These reactive dyes dominated the dyeing industry, despite their low color strength and high cost. Most of the anthraquinone dyes are based on bromaminic acid that is treated with a reactive amine component [15]. An example of these dyes is represented in Figure 2.14.

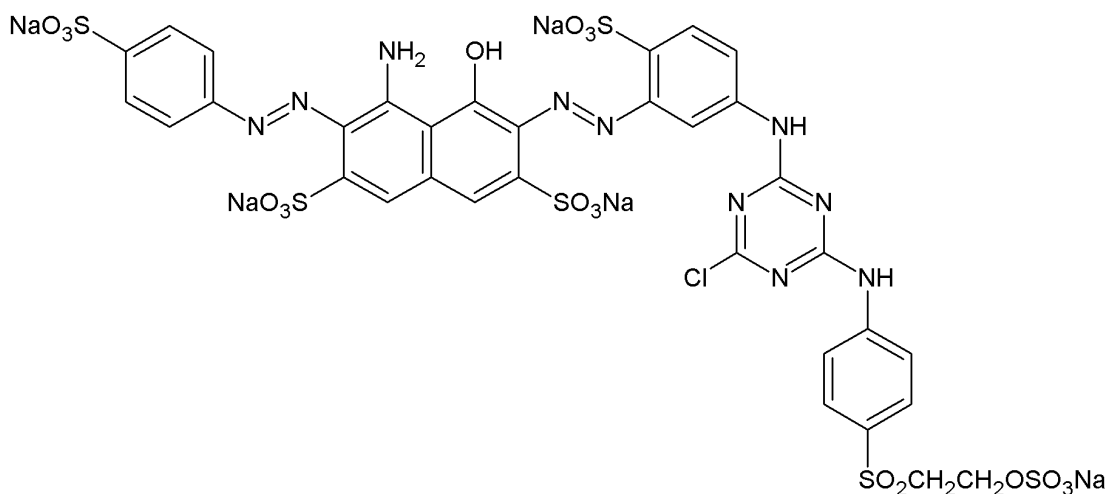


**Figure 2.14 :** Chemical structure of CI Reactive Blue 4 [17].

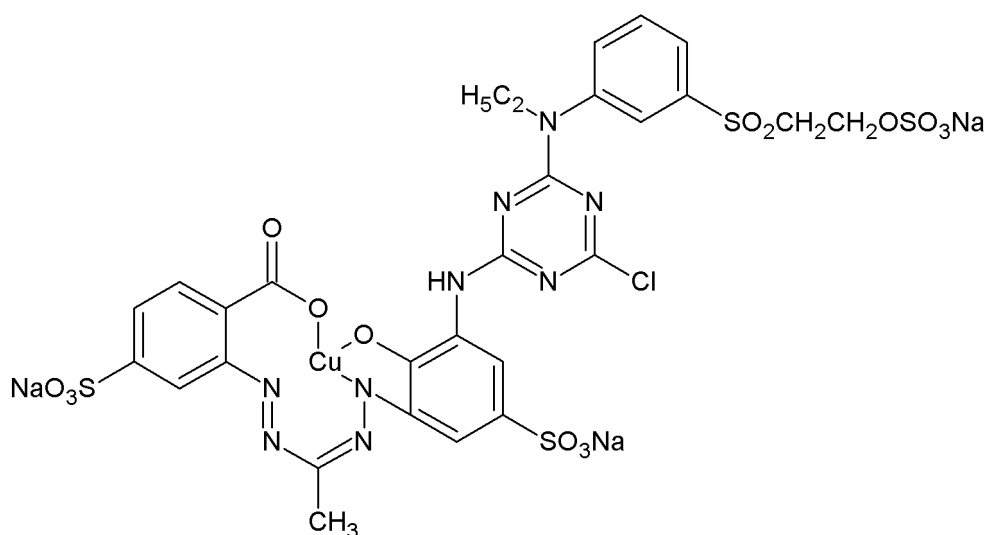
Triphenodioxazine dyes have been marketed since 1928. Adding of sulfonic acid groups to triphenodioxazine ring system generated these reactive dyes. By changing the substituents on the main structure, various colors can be generated. This chromophore group has high substantivity that causes problems such as insufficient levelness, tailing or limited color removal of unfixed dye [14,15]. An example of triphenodioxazine reactive dyes is given in Figure 2.15.

Formazan dyes have copper complexes and are alternative to anthraquinone dyes for generating green to blue shades. Because of the molecular structure of these dyes,

their reactivity and solubility are high. CI Reactive Blue 221 is an example of this type of dyes (see Figure 2.16) [15].

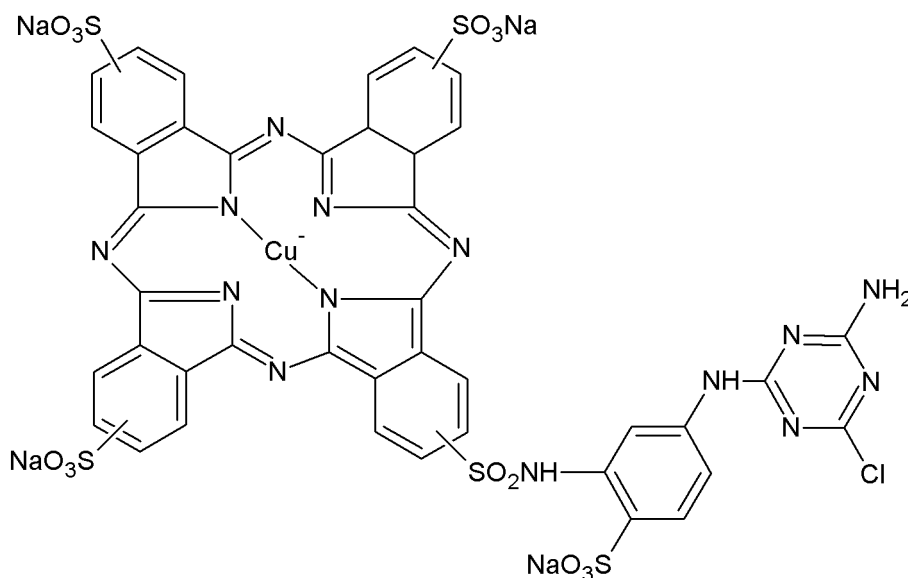


**Figure 2.15 :** Chemical structure of CI Reactive Blue 198 [15].



**Figure 2.16 :** Chemical structure of CI Reactive Blue 221.

Phthalocyanine dyes can produce turquoise and green hues that not available from azo or anthraquinone dyes. The most important phthalocyanine dyes are dominated by central copper and nickel atoms. An example of these reactive dyes is given in Figure 2.17 [15].



**Figure 2.17 :** Chemical structure of CI Reactive Blue 15 [15].

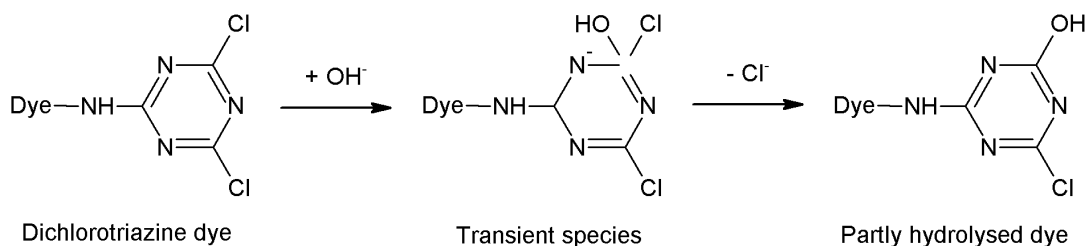
### 2.2.5 Dyeing mechanism of reactive dyes

The reactive dyeing mechanism of reactive dyes can be subdivided into following steps [18]:

- Movement of dye molecules from the dyebath to the cellulose,
- Sorption of dye molecules onto the cellulose surface,
- Permeation (diffusion) of adsorbed dye molecules away from the surface into the microstructure of cellulose,
- Reaction between dye molecules and cellulosate anions in alkaline media,
- Reaction between dye molecules and water in alkaline media,
- Sorption of hydrolyzed dye from the dyebath,
- Hydrolysis of sorbed dye on the cellulose surface.

The biggest handicap of the reactive dyes is that they undergo a hydrolysis reaction that contains reaction of the dye with hydroxide ions present in the alkaline dyebath conditions in competition with the dye-fiber reaction. The hydrolysed dye is incapable of reaction with the cellulose. Therefore, any unreacted and hydrolysed dye must be washed out of fiber after dyeing to ensure the excellent fastness properties. Also, hydrolysis of the dye reduces the degree of fixation. Increase in the hydrolysed and unreacted dyes in dyehouse effluent raises the environmental concerns [6,17]. The hydrolysis reaction is illustrated in Figure 2.18.





**Figure 2.18 :** Hydrolysis reaction of dichlorotriazine dye [5] .

## 2.2.6 Kinetics of reactive dyeing

To simplify the kinetics of the reactive dyes, two models were offered. First model is homogeneous system in which reaction of dyes with alcohol and second one is heterogeneous system in which reaction of dyes with cellulose [13].

### 2.2.6.1 Homogeneous system – water and alcohol

The homogeneous system where reactive dye is present in alcohol solution to understand the guideline of dyeing. The two competing reactions are [13]:

- Alcoholysis of the dye:  $D + AO^- \rightarrow DOA$
- Hydrolysis of the dye:  $D + OH^- \rightarrow DOH$

The concentrations of the products formed at any given time are the ratio of the reaction rates. The efficiency ratio of alcoholysis reaction,  $E$ , is ratio of the rate of alcoholysis and the rate of hydrolysis (2.1).

$$E = \frac{-d[A]/dt}{-d[H]/dt} = \frac{k_A[AO^-]_t[D]_t}{k_H[OH^-]_t[D]_t} = \frac{k_A[AO^-]_t}{k_H[OH^-]_t} \quad (2.1)$$

where  $k_A$  and  $k_H$  are reaction rate constants for alcoholysis and hydrolysis.

The ratio ( $R_A = k_A / k_H$ ) is a constant for a given alcohol and dye, so this equation can be written (2.2):

$$E = R_A \frac{[AO^-]}{[OH^-]} \quad (2.2)$$

The rate of disappearance of active dye molecules at any time can be determined by the sum of the rates of these competing reactions. The disappearance of active dye can be formulated as follows (2.3):

$$\frac{d[D]}{dt} = k_H' [D]_t \quad (2.3)$$

where  $k_H' = k_H (R_A [AO^-]_t + [OH^-]_t)$ .

### 2.2.6.2 Heterogeneous system – water and cellulose

The heterogeneous system of water and cellulose is more complicated than the homogeneous system, because the reactions proceed at different rates within two phases. Dye and cellulose are present in the same phase in the two-phase system, so the dye has to be absorbed into the cellulose before the reaction between dye and cellulose [13].

The rate of sorption of reactive dye per unit area of surface (the rate of fixation) for the dyeing of an infinitely thick slab of material in a dyebath solution with infinite volume can be formulated as follows (2.4):

$$\frac{dQ}{dt} = [D]_F \sqrt{D k_F'} \quad (2.4)$$

where  $[D]_F$  is the concentration of dye at the surface of material,  $D$  is the diffusion coefficient of the dye and  $k_F'$  is the first-order reaction constant for the reaction between dye and substrate.

The efficiency of fixation,  $E$ , is the rate of fixation over the rate of hydrolysis (2.5):

$$E = \frac{S [D]_F \sqrt{D k_F'}}{L [D]_S k_H'} \quad (2.5)$$

where  $[D]_S$  is the concentration of dye in the aqueous phase,  $k_F'$  is the first-order reaction constant of hydrolysis,  $S$  is the surface area of substrate and  $L$  is the liquor ratio. It can be easily seen that the efficiency of fixation is proportional to substantivity ( $[D]_F / [D]_S$ ) and diffusion coefficient [18].

### 2.2.7 Adsorption isotherms

The adsorption isotherms can be expressed as the variation in the concentration of dye absorbed on the fiber surface with the concentration of dye in the liquid when the dyeing is at equilibrium. The curves of adsorption isotherms are illustrated by

plotting the adsorbed dye concentration against the concentration of the dye in the liquor at constant temperature. The adsorption isotherms are useful elements to understand the dyeing kinetics. Most of the dyeing adsorption isotherms can be fitted to three common equations, known as Nernst, Langmuir and Freundlich isotherms respectively [3,6,19-21]. The simplest one is the Nernst isotherm and is formulated by the following equation (2.6):

$$D_F = k D_S \quad (2.6)$$

where  $D_F$  and  $D_S$  are the concentrations of dye in the fiber and in the solution respectively, and  $k$  is the constant. This equation is also the partition of a solute between two immiscible solvents. The plot of  $D_F$  against  $D_S$  is a straight line curve which ends at the point corresponding to the dye saturating the fiber and the water.

The Langmuir adsorption isotherm assumes that adsorption of the dye takes place on limited sites in the fiber, and the fiber becomes saturated with dye, when all sites are occupied and incapable of further adsorption. The rate of desorption is determined by the fraction of occupied sites ( $D_F / D_{max}$ ). At the same time, dye is reaching on the fiber surface from the solution and some of them are adsorbed. The rate of adsorption of dye is determined by the fraction of unoccupied sites ( $1 - D_F / D_{max}$ ) and the concentration of dye in the solution ( $D_S$ ). At equilibrium, the rates of adsorption and desorption are equal (2.7):

$$k_1 \left( 1 - \frac{D_F}{D_{max}} \right) D_S = k_2 \frac{D_F}{D_{max}} \quad (2.7)$$

where  $k_1$  and  $k_2$  are the rate constants for adsorption and desorption and  $D_{max}$  is the maximum number of adsorption sites in the fiber. This can be inverted to (2.8):

$$\frac{D_S}{D_F} = \frac{D_S}{D_{max}} + \frac{1}{K D_{max}} \quad (2.8)$$

where  $K$  is equal to  $k_1 / k_2$ . When  $D_S$  is plotted versus  $D_F$ , the curve becomes parallel with the  $D_S$  axis, once all sites are occupied.

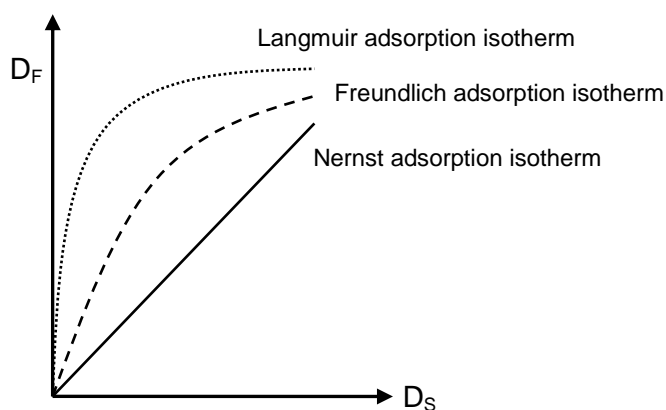
There is no limit for the number of specific adsorption sites in the fiber in case of Freundlich isotherm. Therefore, the fiber is not saturated with dye. The only

limitation is available pore surface area. Dye molecules absorb rapidly initial stage because of the high numbers of accessible pore. However, subsequently dye adsorption becomes slower, because dye molecules have to access to the more remote accessible areas. The empirical equation for this type of isotherm can be expressed as (2.9):

$$D_F = kD_S^x \quad \text{or} \quad \log(D_F) = \log(k) + x \log(D_S) \quad (2.9)$$

where  $k$  is a constant and  $x$  is a fractional power.

The curve of  $D_F$  against  $D_S$  is not linear up or does not react to the point in which it becomes parallel with the  $D_S$  axis. Graphical representation of adsorption isotherms are illustrated in Figure 2.19.



**Figure 2.19 :** Curves for three types of adsorption isotherm [6] .

## 2.2.8 Factors affecting reactive dyes

### 2.2.8.1 Effect of electrolyte

Generally, reactive dyes have little affinity for cotton. Addition of electrolytes to dyebath increases the exhaustion of reactive dyes onto cellulose. Wet cotton fibers create a negative surface potential that repels the dye anions. The sodium ions of electrolyte remove the potential barrier on charged fiber, so the dye anions can reach the cellulose surface to form the chemical bonds between dye and cellulosic fiber. However, high electrolyte concentrations have a negative effect on reaction due to the aggregation of dye solution. Common salt (sodium chloride) is widely used, Glauber's salt (hydrated sodium sulphate) is preferred with certain bright blue or green shades. Electrolyte must be free from alkali, since alkali causes premature fixation or hydrolysis of the dye [5,18,20].

#### **2.2.8.2 Effect of alkali**

Most of the reactive dyes performed well under alkaline dyeing conditions. Addition of alkali leads to formation of covalent bonds between reactive dye and cotton, thus increasing the rate of fixation. Increase in pH to 11 increases the exhaustion and reactivity, but beyond this level, exhaustion decreases. Excessive amount of alkali in dyebath promotes the hydrolysis of dye. Under alkaline conditions, cellulose turns to cellulosate ions. These ions can attack an electron deficient carbon atom of, such as triazine dye to form a covalent bond. The addition of alkali is also necessary for conversion of precursor of vinylsulphone dyes. The most widely used alkali for reactive dyeing is soda ash (sodium carbonate) [16,22].

#### **2.2.8.3 Effect of liquor ratio**

Dyebath exhaustion increases as the dye concentration in the dyebath becomes greater, in other words liquor ratio decreases. Therefore, liquor ratio is a significant variable for the amount of waste dye in the effluent. Lower liquor ratios allow less hydrolysis in reactive dyeing as well as more percentage fixation. However, lowering liquor ratio too much can cause uneven dyeing because of the high dye concentration and high strike ratio [6,20,22-24].

#### **2.2.8.4 Effect of temperature**

Increase in dyeing temperature decreases the substantivity ratio and enhances the rate of hydrolysis. Changing both of them can cause a decrease in fixation efficiency. The temperature of the dyeing procedure is dependent on the type of dye. The low temperatures can be used for dichlorotriazine reactive dyes because of their high reactivity levels. The less reactive types, such as monochlorotriazine reactive dyes, need higher temperature to accelerate the reaction [5,6,25].

#### **2.2.9 Application techniques for reactive dyes**

A wide range of reactive dyes is available which are suitable for many different applications. Generally, reactive dyes undergo reaction with cotton under alkaline conditions, but there are some exceptions. The applicability of a reactive dye according to a specific technique depends not only on its reactivity, but also on characteristics such as substantivity, solubility and diffusion [15].

The reactive dyeing techniques can be divided into two main categories of batch (exhaust) dyeing and continuous (pad) dyeing processes.

Batch dyeing is a popular method for application of reactive dyes to cellulosic fibers including circulating liquor machines for yarn or fabric, as well as jets, jiggers or winches. A typical batch dyeing process has three phases [5]:

- Dye exhaustion from a neutral dyebath in the presence of electrolyte,
- Fixation of the dye is achieved by addition of alkali to the dyebath,
- Washing off reactive dyed textile material to remove all of the unfixed dye and residual electrolyte and alkali.

In continuous dyeing processes, fabrics are padded into dyebath and then passed through the squeezing rollers to remove the excess liquor. Fixation of dye is accomplished in a subsequent step. The main advantages of these processes are low water consumption and reduced effluent because of the small liquor ratios, more consistency in dyeing quality and high productivity [15].

### 2.3 Dyebath Monitoring Systems

Determination of the dye concentration in solution is critical in order to achieve the controlling the all dyeing process [26,27]. The ability to monitor dye concentrations can be used for optimization of production efficiency, improved product quality and detection of errors [28,29]. To effect a high level of control over any dyeing process, it is necessary to monitor the profile of the exhaustion curves of each dye that forms the dyeing recipe [30]. Therefore, it is essential to calculate the current concentration of dye in the dyebath over entire entire dyeing process [27]. This task is generally achieved by analytical evaluation of dyebath samples using spectrophotometry according to Beer-Lambert law [31] which can be expressed by (2.10):

$$A = \log(I_0/I) = \epsilon c l \quad (2.10)$$

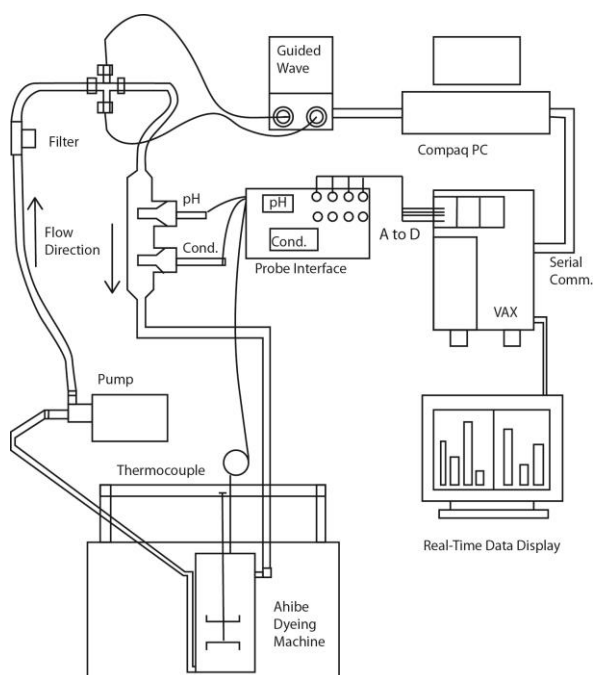
where  $A$  is the absorbance of a dye at a particular wavelength,  $I_0$  is the intensity of light incident on the sample and  $I$  is the transmitted light intensity. In the alternative notation of absorbance,  $c$  is the dye sample concentration,  $l$  is the path length and  $\epsilon$  is the molar extinction coefficient (or molar absorptivity) [26].

The direct application of the Beer-Lambert law for determining the dye concentration can be difficult because of the certain reaction conditions. These can occur as a result of changes in the state of dye, as a function of concentration, temperature and pH [27]. In these conditions, dye concentration can no longer be calculated using the Beer-Lambert law, since absorbance characteristics (i.e. extinction coefficients) of the dyes in the dyebath change throughout the dyeing process [32].

In order to overcome these difficulties, two approaches were established. In the first approach, the concentration of dye is directly measured. The effects of temperature, pH and dye concentration on the extinction coefficient of the dye must be predicted and taken into account in the conversion from absorbance to concentration values. The second attempt (flow or sequential injection analysis) aims at bring the dyebath sample to standard conditions that allow an accurate and precise analysis before the absorbance measurement. The control of temperature, pH and dye concentration is also necessary [33].

### 2.3.1 Direct dyebath monitoring system

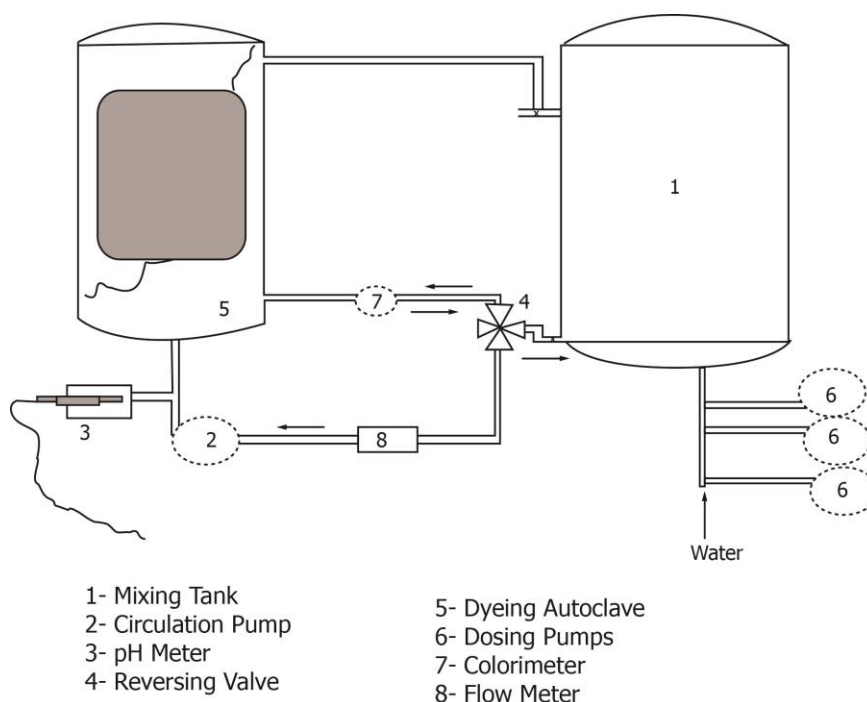
A group of researchers at North Carolina State University developed a direct dyebath monitoring system (as shown in Figure 2.20) that measures pH, conductivity, temperature and dye absorbance of the dyebath in real-time [32,34].



**Figure 2.20 :** Schematic diagram of direct dyebath monitoring system [34].

The exhaustion curves were also displayed. In this system, circulating and sampling tool transported the dyebath through pH, conductivity and a fixed path length absorbance probes. The absorbance values at appropriate wavelengths were converted to concentration and exhaustion data using Beer-Lambert law for single dyes and multiple linear regression [35] or neural networks [36] for dye mixtures.

Another direct dyebath monitoring system was developed by researchers at University of Leeds (see Figure 2.21). Gilchrist and Nobbs [30] developed an analysis system based on an in-line optical cell with linked to a computer based match prediction system which included compensation for changes in dyebath temperature. A multiple path length cell was used to overcome problems associated with Beer-Lambert law, therefore accurate concentration measurements were possible. A reflectance cell was installed directly to the dyeing machine, thus avoiding the need for any sampling mechanism. The inverse Laplace transform was used to derive path length distribution of the cell from a measured variation of reflectance with concentration. In the second part of their studies [38], the control algorithms were proposed to explain the relationship between dyebath temperature and exhaustion rate of a basic dye at acrylic dyeing. The time averaging methods were used to decrease the variations in the calculation of the exhaustion rate.



**Figure 2.21 :** Schematic diagram of dyebath monitoring system developed at University of Leeds [39].



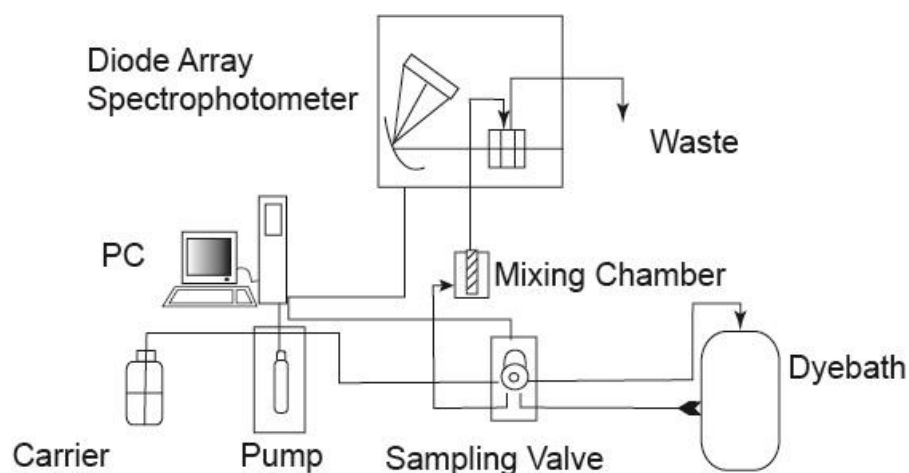
Shamey and Nobbs [39] developed a reliable control system for the reactive dyeing of cellulosic fibers using a pilot scale package dyeing machine monitored by a computerized data logging and control system. This setup was similar with the system developed by Gilchrist and Nobbs. Shamey and Nobbs [40] also established a close-loop feedback control system to control pH in the dyebath. The method was based on the use of preset pH profiles. The temperature dependence of system and the effect of dye and auxiliaries in the dyebath were investigated. The requirement for simplifications was found to use this system under dynamic conditions. A feed-forward control algorithm based on the use of preset exhaustion profiles was proposed by Shamey and Nobbs [41]. Various parameters including dye concentration and pH in the dyebath were monitored. Mathematical models were derived to explain the conditions of the dyeing process at any time.

### **2.3.2 Flow injection analysis system**

Flow injection analysis (FIA) is a simple and versatile technique for various applications in quantitative chemical analysis. Ruzicka and Hansen [42] developed FIA in 1975. The concept of FIA is based on the following factors: reproducibility of sample injection volumes, reproducible timing of the injected sample through the flow system and controlled sample dispersion [43]. In FIA, a liquid sample is injected into a moving nonsegmented carrier stream. The injected sample creates a zone in which the sample disperses and reacts with the components of the carrier stream, forming a chemical species to be measured by a flow through detector (for measurement of dye concentration, it is a spectrophotometer). Its typical data is a peak whose height is related to the sample concentration [44].

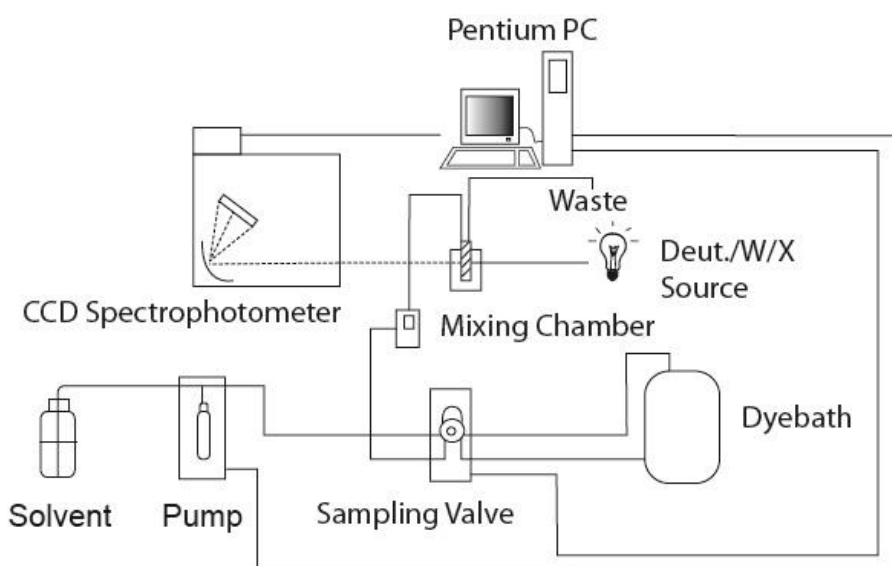
To overcome the limitations of the direct dyebath monitoring systems, FIA was employed for online monitoring by researchers at North Carolina State University for reactive [45] and disperse [46] dyes. A schematic diagram of the FIA system used to monitor reactive and disperse dyeings is represented in Figure 2.22. A calibration model for a trichromatic reactive dye mixture based on the Beer-Lambert law was developed. However the measurements were made on dye mixtures instead of individual dyes. This law could not be applied directly. Therefore, partial least square method was used to generate reliable calibrations for conversion of absorbance to individual concentrations in dye mixture [45]. When FIA was used to monitor

disperse dyes, the carrier would be a suitable solvent that was capable of dissolution of the both nonpolar disperse dyes and polar dispersing agent. Good results were achieved with a 70/30 mixture of acetone and water [46].



**Figure 2.22 :** Schematic diagram of FIA dye bath monitoring system used for reactive and disperse dyeings [46].

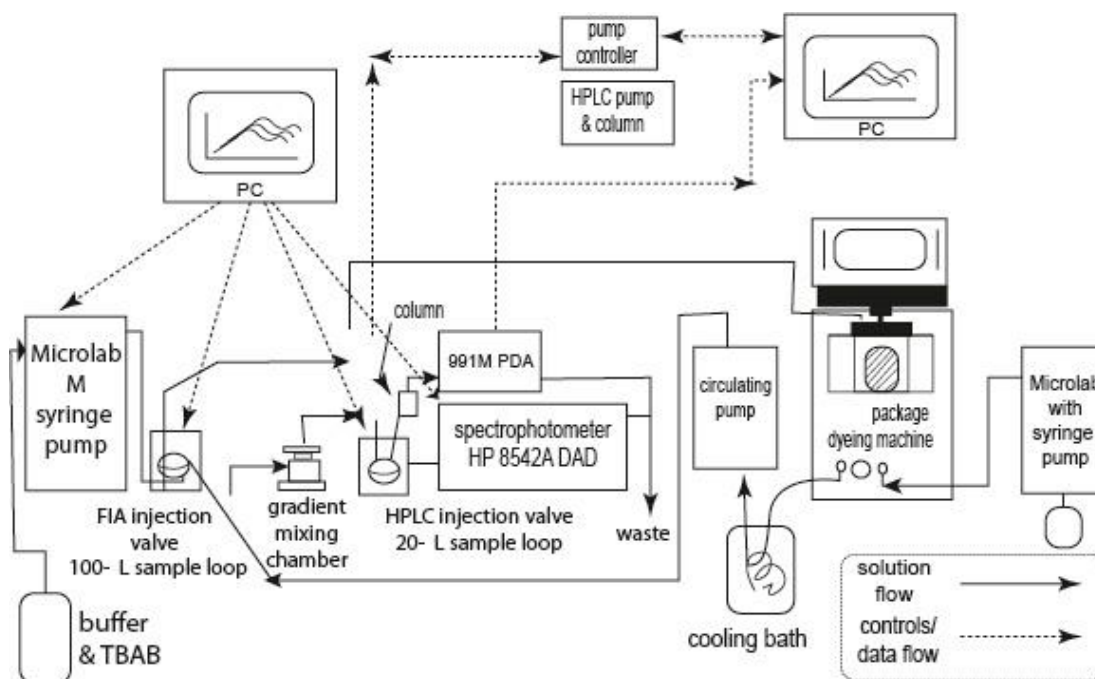
A comparison of FIA and redox titration methods for monitoring indigo in the dyebaths was reported [47]. FIA provided the more rapid, precise and accurate measurements for indigo concentration than titration methods. A schematic diagram of the FIA system is shown in Figure 2.23.



**Figure 2.23 :** Schematic diagram of FIA dye bath monitoring system used for indigo dyeings [47].

In order to measure the hydrolysis of reactive dyes, a high performance liquid chromatography (HPLC) separation system was integrated to FIA [48]. HPLC separated reactive dyes into hydrolysed and reactive components. The combination

of FIA and HPLC was used for real-time monitoring of both the degree of hydrolysis and exhaustion of reactive dyes. A schematic diagram of FIA-HPLC system is given in Figure 2.24.



**Figure 2.24 :** Schematic diagram of FIA-HPLC system [48].

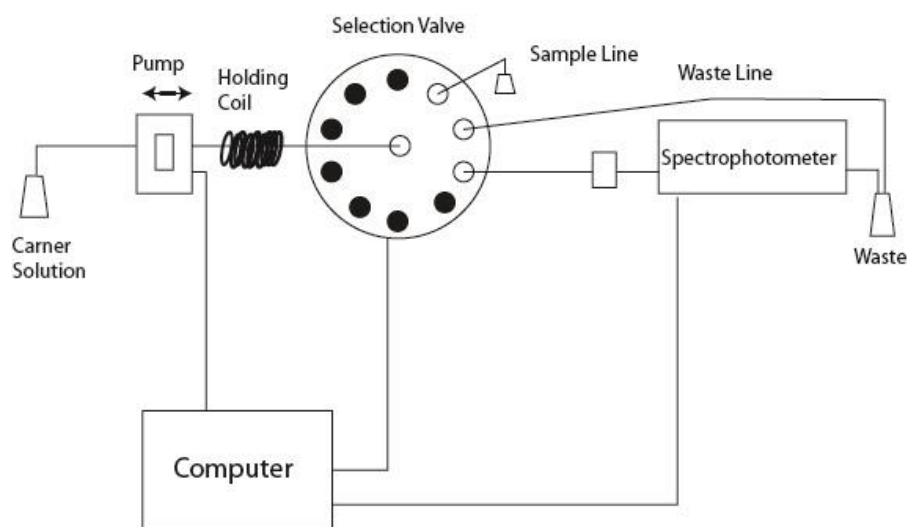
FIA was also applied for monitoring of direct [49] and acid [50] dyeings of cationized cotton. It was found that FIA was a useful method for understanding the effect of the cationic pretreatment on dye uptake for both direct and acid dyes.

### 2.3.3 Sequential injection analysis system

Sequential injection analysis (SIA) was developed by Ruzicka and Marshall [51] in 1990. It is an alternative technique for analytical chemistry in order to eliminate the main drawbacks of FIA which are manual reconfiguration of flow channel, high reagent consumption, frequent servicing of peristaltic pumps and continual recalibration of system [52]. Whereas a sample is injected into a flowing carrier and reagents mixed with it on the way to the detector, SIA is based on different approach. By using a selection (rather than injection) valve, the sample and reagent zones are subsequently aspirated into a channel to subsequently reverse the flow and transport the stacked zones into the detector [53].

A dyebath monitoring system based on the principles of SIA was developed for analysis of batch dyeing processes [54]. The SIA and FIA systems were compared in terms of accuracy of dye concentration measurements. Dyebath monitoring

experiments with SIA gave the same precision as those of FIA and overall correlation between the two systems very good. A schematic diagram of SIA dyebath monitoring system is represented in Figure 2.25.



**Figure 2.25 :** Schematic diagram of SIA dyebath monitoring system [54].

### 2.3.4 Other dyebath monitoring systems

A real-time dyebath monitoring system was developed to determine the multiple dye concentrations for carpet dyeings [26,29]. The dyebath sample was pumped to a flow cell by a gradient HPLC pump, which allows precise dilution of the sample for spectrophotometric analysis. Using an exponential model for treating the relationship between absorbance and dye concentration yielded much higher accuracy than a linear model.

Huang and Yu [55] proposed an approach to control dye concentration, pH and temperature in the dyebath using with a fuzzy logic controller. The results showed that the fuzzy control was able to control the dyeing parameters at the desired values.

In order to monitor the indigo dyeings, a laser diode spectrometer integrated with a dilution system was designed [56]. This system offered some advantages such as stable indigo solution in the mixing tank, no need for nitrogen atmosphere and no interference due to sulphur compounds.

Dyebath analysis was used for optimizing the dyeing of polyester with disperse dyes [57]. It was found that, the process profiles depended on machine type, because the maximum temperature gradient varied from one machine to another machine.

An automated system was used to monitor the specific absorptivity of the reactive dyes during the dyeing process [27]. The relationship between the type of reactive group and the visible spectral changes over time was investigated. The spectral shifts depended directly on the nature of the reactive group and chromogen.

An alternative method based on colorimetric sensors to the typical spectrophotometric analysis was developed for real-time monitoring of dyebath exhaustion [58]. Optical fibers were used as colorimetric sensors for the transmission of measured values. A luminous flow was sent into a measuring chamber where circulated the dyebath. Then, the light flow was analyzed by four optical filters to cover all the visible spectrum. In another study which used an optical fiber sensing system, an online monitoring system was designed for in-situ measurement of reactive dye concentration [59]. The optical fiber sensors were proved to be applicable to determine the dye concentrations of single dyes and mixtures with two dyes.



### **3. EXPERIMENTAL**

#### **3.1 Materials**

##### **3.1.1 Fabric**

The fabric used in this study was a 100% standard single jersey knitted cotton fabric. The fabric weight was measured as 121.0 g/m<sup>2</sup>.

##### **3.1.2 Chemicals**

All solution percentages are expressed as weight on weight.

Chemicals used for bleaching:

- Hydrogen Peroxide: Reagent grade,
- Sodium Carbonate: Reagent grade,
- Stabilizer: Clarite G-100, Huntsman Chemicals Company.

Chemicals used for the diluent:

- Sodium Acetate: Fisher Chemicals Company,
- Acetic Acid: Glacial, 99.8%, Fisher Chemicals Company.

Chemicals used for dyeing:

- Reactive Dyestuff: C.I. Reactive Red 238, Novacron Red FN-R, Huntsman Chemicals Company,
- Reactive Dyestuff: C.I. name not available, Novacron Brilliant Red FN-3GL, Huntsman Chemicals Company,
- Reactive Dyestuff: C.I. Reactive Yellow 206, Novacron Yellow FN-2R, Huntsman Chemicals Company,
- Reactive Dyestuff: C.I. name not available, Novacron Navy FN-GN, Huntsman Chemicals Company,
- Sodium Sulfate (Glauber's Salt): Reagent grade,

- Sodium Carbonate: Reagent grade,
- Soaping Agent: Triton X-100, Dow Chemicals Company.

## 3.2 Equipments

### 3.2.1 Stirring hot plate

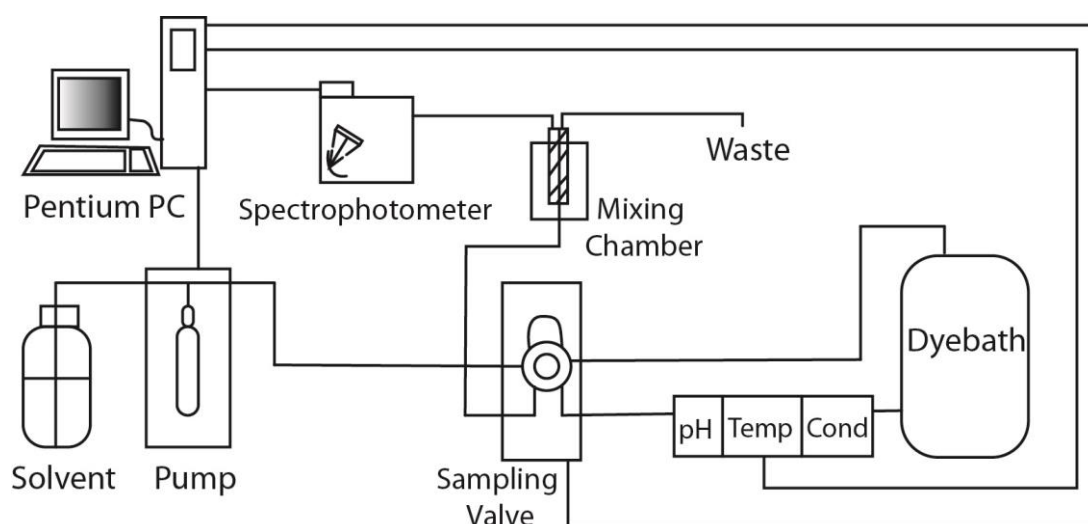
A Fisher Hot Plate was used to control the heating and stirring during preparation of dyebath solution.

### 3.2.2 Dyeing machine

Dyeing process was performed using a Datacolor AHIBA MULTIPRECISE TC type laboratory dyeing machine.

### 3.2.3 Dyebath monitoring system

The FIA dyebath monitoring system developed by HueMetrix was used for all monitoring experiments (see Figure 3.1). This system included a 48000-step Kloehn® 50300 syringe pump, a two-position Valco® EMHMA-CE selection valve, a Mintek® gradient mixing chamber, an Ocean Optics® SD1000 fiber optic spectrophotometer and a Pentium PC. System control and data acquisition were controlled using the the software developed by HueMetrix.



**Figure 3.1 :** Schematic diagram of dyebath monitoring system.



### 3.3 Testing

#### 3.3.1 Determination of percent exhaustion and fixation

Spectrophotometric analysis was used to determine the amount of dye in the dyebath before and after dyeing as well as in the wash-off solutions. Percent dye exhaustion (%E) achieved for each dye was calculated as follows (3.1):

$$\%E = \frac{C_0 - C_1}{C_0} \times 100 \quad (3.1)$$

where  $C_0$  and  $C_1$  are the concentrations of dye before and after dyeing, respectively. For each dye, percentage dye fixation (%F), which is the percentage of the dye absorbed to the fabric becoming covalently bonded, was calculated as follows (3.2):

$$\%F = \frac{C_0 - C_1 - C_2}{C_0 - C_1} \times 100 \quad (3.2)$$

where  $C_0$ ,  $C_1$  and  $C_2$  are the respective concentrations of the dye before ( $C_0$ ) and after ( $C_1$ ) dyeing and in the wash-off solutions ( $C_2$ ). To determine the concentration of the dye in the wash-off solutions ( $C_2$ ), samples from each of the wash-off stages, which were described above, were analyzed with real time monitoring device, thus it is possible to determine the dye amount in the wash-off solutions.

#### 3.3.2 Color measurement

The colorimetric values of dyed fabric samples were measured on a Datacolor Spectraflash SF600X spectrophotometer (Datacolor International) using D65 illuminant, 10° Standard supplementary observer and 30 mm aperture. The ultraviolet (UV) component was excluded and the specular component was included. After folding the samples twice to ensure opacity, four measurements were taken from each sample with a 90° sample rotation before each measurement. The average of these four measurements was calculated. The  $K/S$  values were obtained from the measurement of the percentage reflectance at  $\lambda_{\max}$ , the wavelength of maximum absorption.

### **3.3.3 Color fastness**

Color fastness to washing was determined according to ISO 105-C06 Colour fastness to domestic and commercial laundering test method. Color fastness to water was determined according to ISO 105-E01 Colour fastness to water test method. Color fastness to perspiration was determined according to ISO 105-E04 Colour fastness to perspiration test method. Color fastness to rubbing was determined according to ISO 105-X12 Colour fastness to rubbing. Color fastness to light was determined according to ISO 105-B02 Colour fastness to light: Xenon arc fading lamp test method.

## **3.4 Applied Processes**

### **3.4.1 Bleaching**

Cotton fabric used for dyeing was bleached at 60°C for 20 min in a solution containing 2 g/L hydrogen peroxide, 2 g/L sodium carbonate and 2 g/L stabilizer with a liquor ratio (L:R) of 1:15. Bleached fabric was rinsed for 10min.

### **3.4.2 Calibration**

Calibration is the process by which the instrument learns to recognize a specific dye and to accurately determine its concentration. Calibrating the instrument is a simple process that requires injection of each calibration solution through an injection port. Since each dye exhibits different spectral characteristics, the system must be calibrated for each individual dye.

Seven calibration solutions were prepared for each dye with concentrations ranging from 0.01 g/L to 1.0 g/L. Calibration solutions cover the range of concentrations expected to occur during the dyeing process. Distilled water and appropriate analytical techniques were used to prepare calibration solutions. Aliquots of 1 g/L stock solutions were diluted to the appropriate volumes (0.01, 0.05, 0.1, 0.25, 0.5, 0.75 and 1.0 g/L).

### **3.4.3 Dyeing**

The amounts of dye required for the shade were measured on an analytical balance and measured dyes were dissolved in ~300 mL of distilled water at 60°C. The amount of electrolyte required for recipe were measured and dissolved in ~600 mL

of distilled water. Dye and electrolyte solution were mixed, and final solution was brought to a volume of 1085 mL with distilled water at room temperature. 200 mL of distilled water at room temperature was used to solve alkali, and alkali solution was added after beginning of dyeing according to procedure to reach the total dyebath volume of 1285 mL.

A commercial trichromatic recipe was employed according to dye manufacturer recommendations. The amounts of dyes used were 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN respectively.

### **3.5 Experimental Design**

Optimization means the study of problems when trying to minimize or maximize a real function by systematically choosing the values of real or integer variables from within an allowed set. It practically means to reach a desired result by using as few as possible resources which means that the final response value that one tries to reach determines the level of factors that are effective on this response in optimization. There are generally more than one combination of factors to reach optimum response and one picks the factor levels that are more beneficial. Since 1980s, increasing ecological concerns brought the need for using less chemicals and energy in all industries. This resulted in studies on developing eco-friendly processes often with optimization.

Response surface methodology is the process of adjusting predictor variables to move the response to an optimum. There are two types of response surface design; Box-Wilson (also known as Central Composite Design) and Box-Behnken. For three factors, the Box-Behnken design offers some advantage in requiring a fewer number of runs. For 4 or more factors, this advantage disappears. In this study, we followed a Box-Wilson Design as we had 4 factors, namely electrolyte concentration, alkali concentration, temperature and waiting time. The central composite design permits a more accurate mathematical model to be produced than the full factorial model and is appropriate for optimization [60]. Among the various types of central composite design, we chose to use a rotatable circumscribed central composite design because of high quality predictions provided over the entire design space. Circumscribed central composite design requires factor settings ( $\pm\alpha$ ) outside the range of the factors

in the factorial part. To maintain rotatability, the value of  $\alpha$  depends on the number of experimental runs in the factorial portion of the central composite design. The values of  $\alpha$  is determined as 2 for a rotatable circumscribed central composite design with five factors. Coded levels of central composite design are given in Table 3.1. Actual levels of central composite design are given in Table 3.2.

**Table 3.1 :** Central composite design in coded level.

| Coded ID | Electrolyte, g/L | Alkali, g/L | Temperature, °C | Waiting time, min |
|----------|------------------|-------------|-----------------|-------------------|
| 1        | -1               | -1          | -1              | -1                |
| 2        | -1               | -1          | -1              | +1                |
| 3        | -1               | -1          | +1              | -1                |
| 4        | -1               | -1          | +1              | +1                |
| 5        | -1               | +1          | -1              | -1                |
| 6        | -1               | +1          | -1              | +1                |
| 7        | -1               | +1          | +1              | -1                |
| 8        | -1               | +1          | +1              | +1                |
| 9        | +1               | -1          | -1              | -1                |
| 10       | +1               | -1          | -1              | +1                |
| 11       | +1               | -1          | +1              | -1                |
| 12       | +1               | -1          | +1              | +1                |
| 13       | +1               | +1          | -1              | -1                |
| 14       | +1               | +1          | -1              | +1                |
| 15       | +1               | +1          | +1              | -1                |
| 16       | +1               | +1          | +1              | +1                |
| 17       | $-\alpha$        | 0           | 0               | 0                 |
| 18       | $+\alpha$        | 0           | 0               | 0                 |
| 19       | 0                | $-\alpha$   | 0               | 0                 |
| 20       | 0                | $+\alpha$   | 0               | 0                 |
| 21       | 0                | 0           | $-\alpha$       | 0                 |
| 22       | 0                | 0           | $+\alpha$       | $-\alpha$         |
| 23       | 0                | 0           | 0               | $-\alpha$         |
| 24       | 0                | 0           | 0               | $+\alpha$         |
| 25       | 0                | 0           | 0               | 0                 |
| 26       | 0                | 0           | 0               | 0                 |

**Table 3.2 :** Central composite design in actual level.

| Coded ID | Electrolyte, g/L | Alkali, g/L | Temperature, °C | Waiting time, min |
|----------|------------------|-------------|-----------------|-------------------|
| 1        | -1               | -1          | -1              | -1                |
| 2        | -1               | -1          | -1              | +1                |
| 3        | -1               | -1          | +1              | -1                |
| 4        | -1               | -1          | +1              | +1                |
| 5        | -1               | +1          | -1              | -1                |
| 6        | -1               | +1          | -1              | +1                |
| 7        | -1               | +1          | +1              | -1                |
| 8        | -1               | +1          | +1              | +1                |
| 9        | +1               | -1          | -1              | -1                |
| 10       | +1               | -1          | -1              | +1                |
| 11       | +1               | -1          | +1              | -1                |
| 12       | +1               | -1          | +1              | +1                |
| 13       | +1               | +1          | -1              | -1                |
| 14       | +1               | +1          | -1              | +1                |
| 15       | +1               | +1          | +1              | -1                |
| 16       | +1               | +1          | +1              | +1                |
| 17       | $-\alpha$        | 0           | 0               | 0                 |
| 18       | $+\alpha$        | 0           | 0               | 0                 |
| 19       | 0                | $-\alpha$   | 0               | 0                 |
| 20       | 0                | $+\alpha$   | 0               | 0                 |
| 21       | 0                | 0           | $-\alpha$       | 0                 |
| 22       | 0                | 0           | $+\alpha$       | $-\alpha$         |
| 23       | 0                | 0           | 0               | $-\alpha$         |
| 24       | 0                | 0           | 0               | $+\alpha$         |
| 25       | 0                | 0           | 0               | 0                 |
| 26       | 0                | 0           | 0               | 0                 |



## **4. RESULTS AND DISCUSSION**

### **4.1 Preliminary Experiments**

#### **4.1.1 Effect of alkali addition and temperature**

In order to analyze the effects of portionwise addition of alkali, addition steps as well as the fixation temperature on exhaustion profiles of individual dyes in admixture in the dyebath, the real time monitoring device was used.

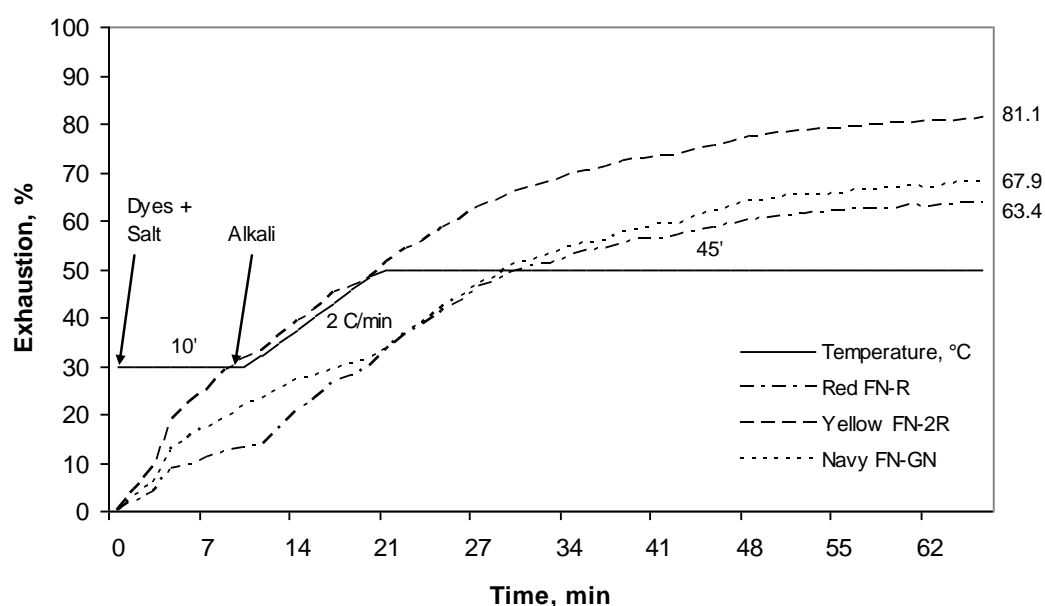
The dyeings were performed at a liquor ratio of 20:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were 60 g/L sodium sulfate and 5 g/L sodium carbonate. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

Each graph contains a straight line, which represents the time-temperature profile for each dyeing. Also other dyeing procedure including dyes, electrolyte and alkali are shown in each graph.

Under alkaline conditions reactive dyes react with hydroxyl groups of cellulose, mostly by nucleophilic substitution or addition, to form the covalent bonds. The dye-fibre covalent bond formation reaction depends on the interrelation between physico-chemical and electro-chemical forces at the cellulose/solution interface; major parameters affecting these interactions include bath pH, electrolyte concentration and dyebath temperature. At the aqueous solution/cotton interface, the surface of the cellulosic fibre acquires a negative charge, mainly because of the dissociation of accessible cellulose hydroxy (Cell-OH) groups. The extent of the dissociation of Cell-OH is clearly affected by the alkalinity of the aqueous medium. Reactive dyeing processes rely on alkali additions to increase the concentration of the nucleophilic Cell-O<sup>-</sup> groups.

In order to investigate the effect of alkali addition in one portion before heating up, we conducted a set of trials by dyeing cotton fabrics at 3 different temperatures (50, 60 and 70°C).

Figure 4.1, 4.2 and 4.3 show the exhaustion profiles of all three dyes used separately. Generally reactive dyes exhibit high exhaustion values, under appropriate application conditions, but it can be seen that Novacron Red FN-R and Novacron Navy FN-GN exhibited relatively low exhaustion values. In addition, the dyes in the dyebath were not compatible each other, although they were recommended to use together.

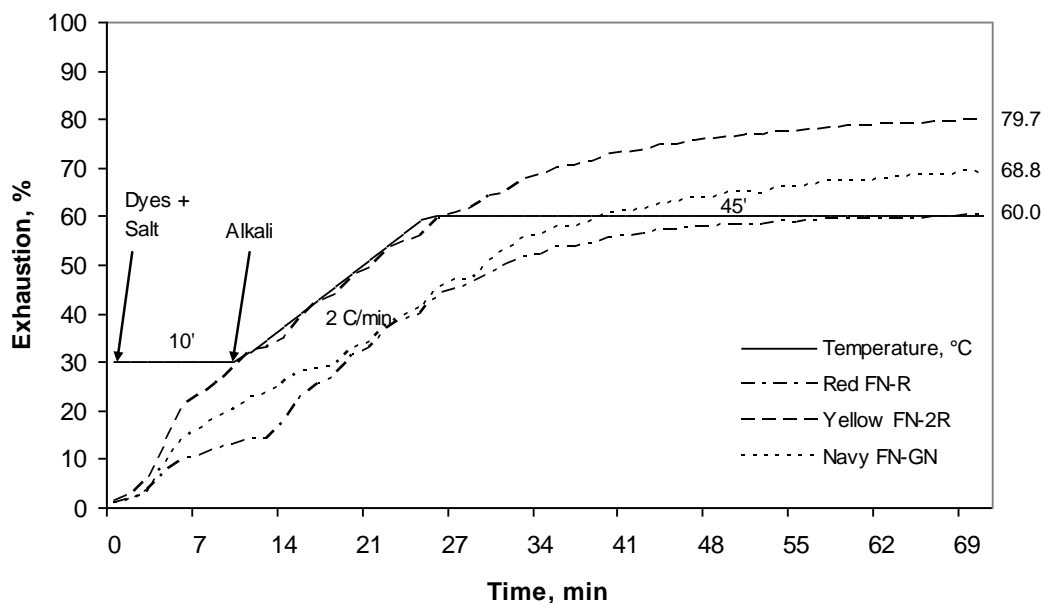


**Figure 4.1 :** The effect of alkali addition in one portion before heating up (50°C).

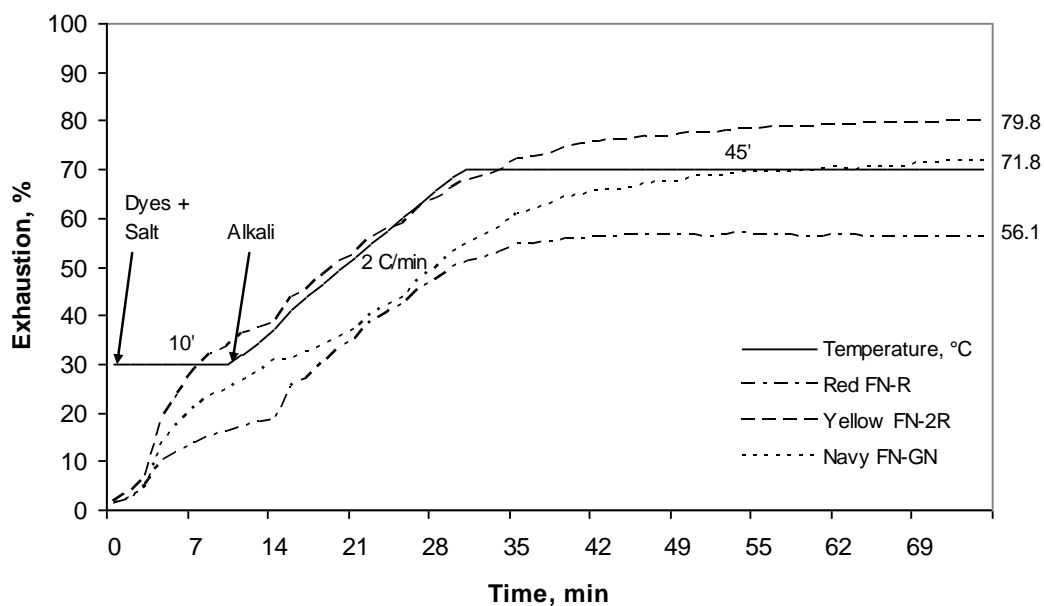
When the temperature was increased from 50 to 60 then 70°C, the exhaustion performance of Novacron Red FN-R decreased progressively, on the other hand, that of Novacron Navy FN-GN increased slightly and Novacron Yellow FN-2R was not affected by changing the temperature. The changing of exhaustion levels was due to an increase in mobility with higher temperature, but a decrease in substantivity and dye uptake.

It can be seen clearly that this dyebath monitoring system is a useful tool for examining the effect of temperature on individual exhaustion property of each dye in dye mixture.





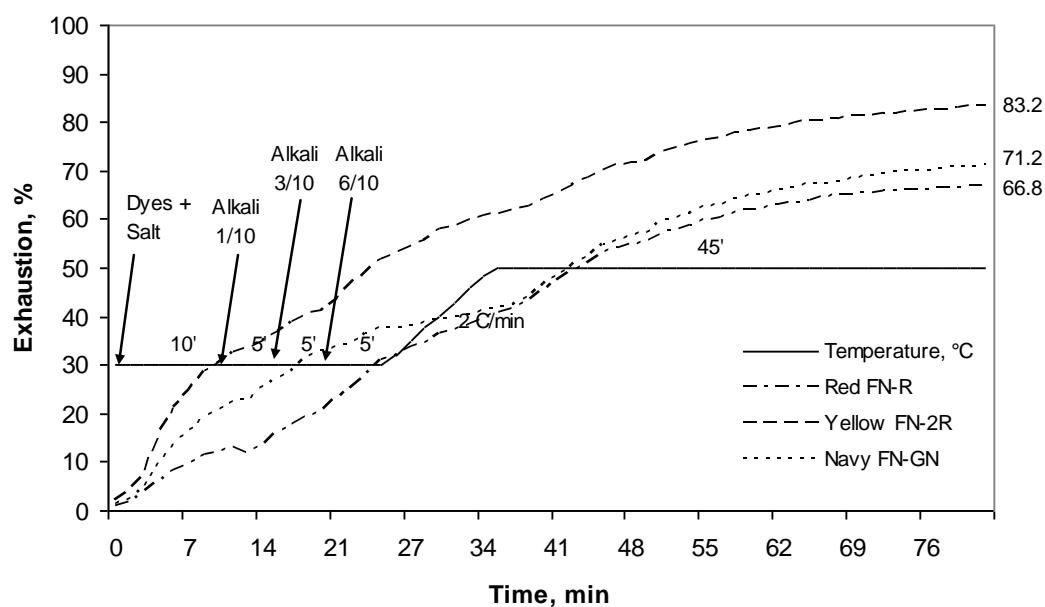
**Figure 4.2 :** The effect of alkali addition in one portion before heating up (60°C).



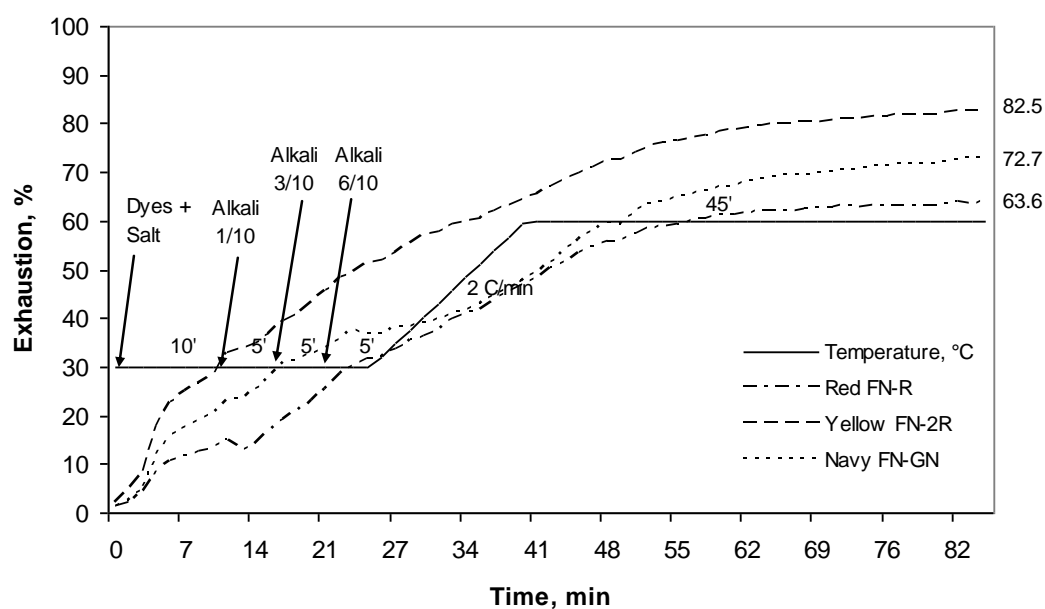
**Figure 4.3 :** The effect of alkali addition in one portion before heating up (70°C).

To control the rate of exhaustion, a dyebath heating process has been used widely as a commercial dyeing process. However, in reactive dyeing process, it is very difficult to control the rate of exhaustion to a required degree by regulating the rate of heating. On the other hand, to control the rate of exhaustion, portionwise addition or dosing of alkali is an effective method and is suitable for an optimized dyeing process.

In order to investigate the effect of alkali addition in three portions before heating up, we conducted a set of trials by dyeing cotton fabrics at 3 different temperatures (50, 60 and 70°C). Figure 4.4, 4.5 and 4.6 show the exhaustion profiles of all three dyes used separately.

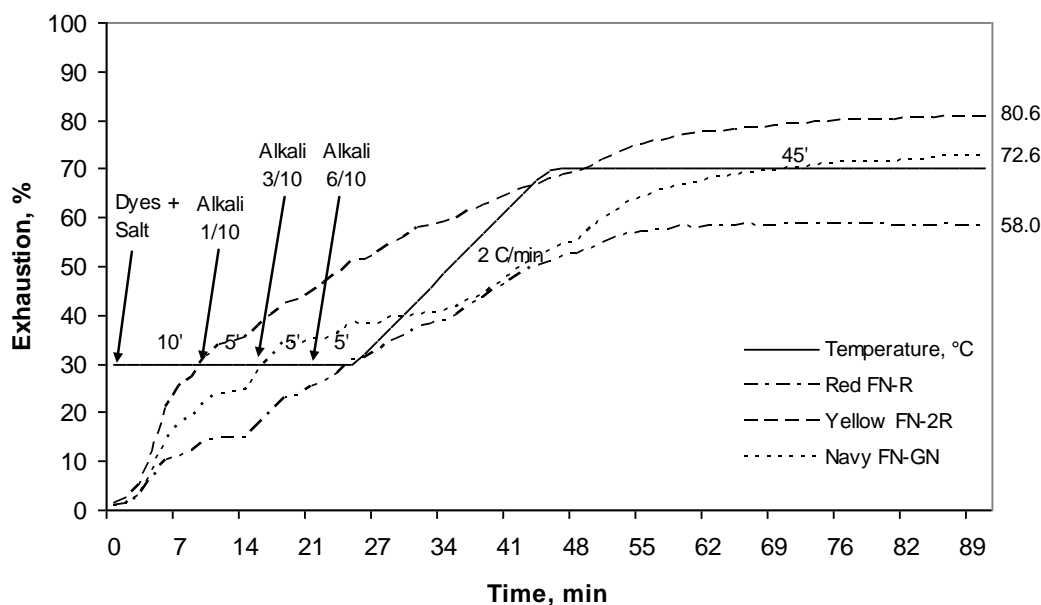


**Figure 4.4 :** The effect of alkali addition in three portions before heating up (50°C).



**Figure 4.5 :** The effect of alkali addition in three portions before heating up (60°C).

From the results, when the portionwise addition of alkali was used, the overall exhaustion values of all dyes are increased in comparison with alkali addition in one portion. It can also clear that, the higher the dyeing temperature the lower the exhaustion values of the dyes for Novacron Red FN-R and Novacron Yellow FN-2R.

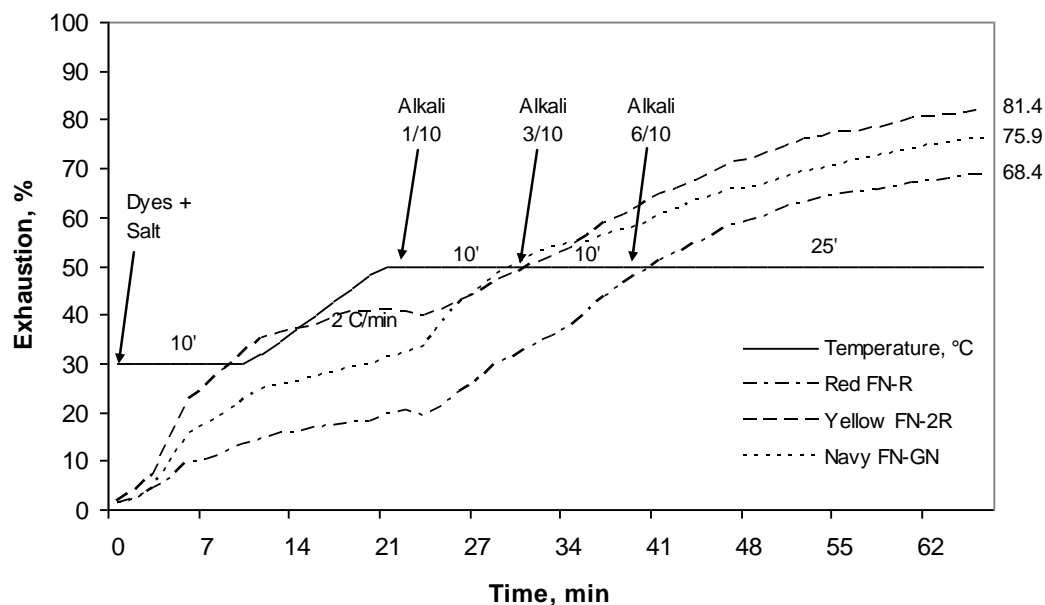


**Figure 4.6 :** The effect of alkali addition in three portions before heating up (70°C).

After confirming that portionwise addition of alkali is more effective than addition of alkali in one portion, we decided to add alkali at fixation step.

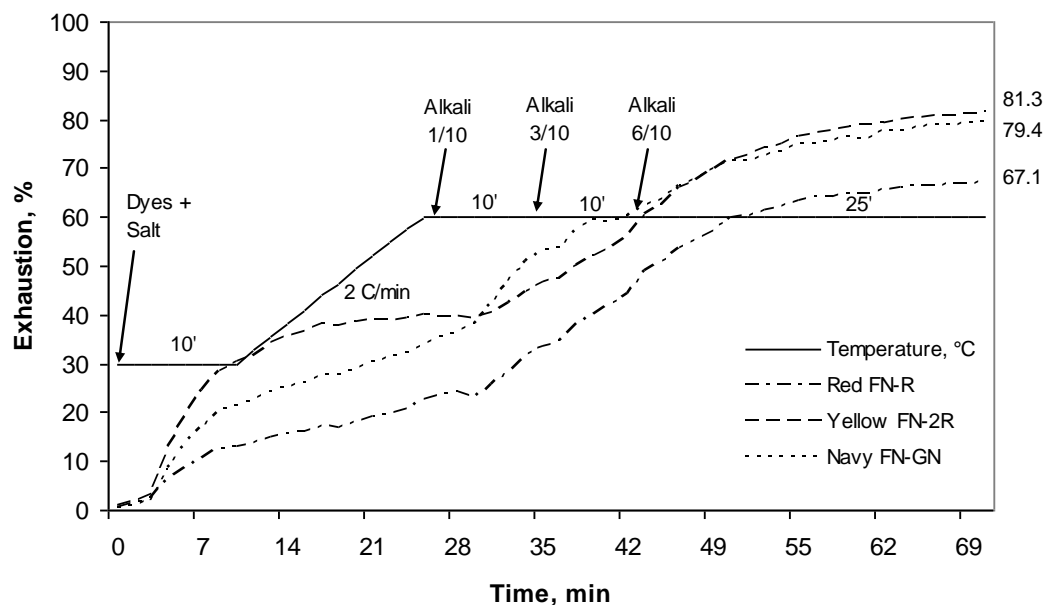
In the typical reactive dyeing procedure, the dyes are commonly applied in two phases: exhaustion and fixation. The exhaustion phase starts in the beginning of dyeing under neutral conditions, and dye uptake reaches to equilibrium in the process of time. The presence of electrolyte also promotes the exhaustion. After the exhaustion phase, the dyebath temperature reaches the certain point (known as fixation temperature) and addition of alkali starts the fixation phase. Cellulose begins to react with the dye in this phase. It is believed that if the alkali is added during the exhaustion phase, it can cause the hydrolysis of dyes which reduces the dyeing performance. In order to investigate the effect of alkali addition in three portions after heating up, we conducted a set of trials by dyeing cotton fabrics at 3 different temperatures (50, 60 and 70°C).

Figure 4.7, 4.8 and 4.9 show the exhaustion profiles of all three dyes used separately.

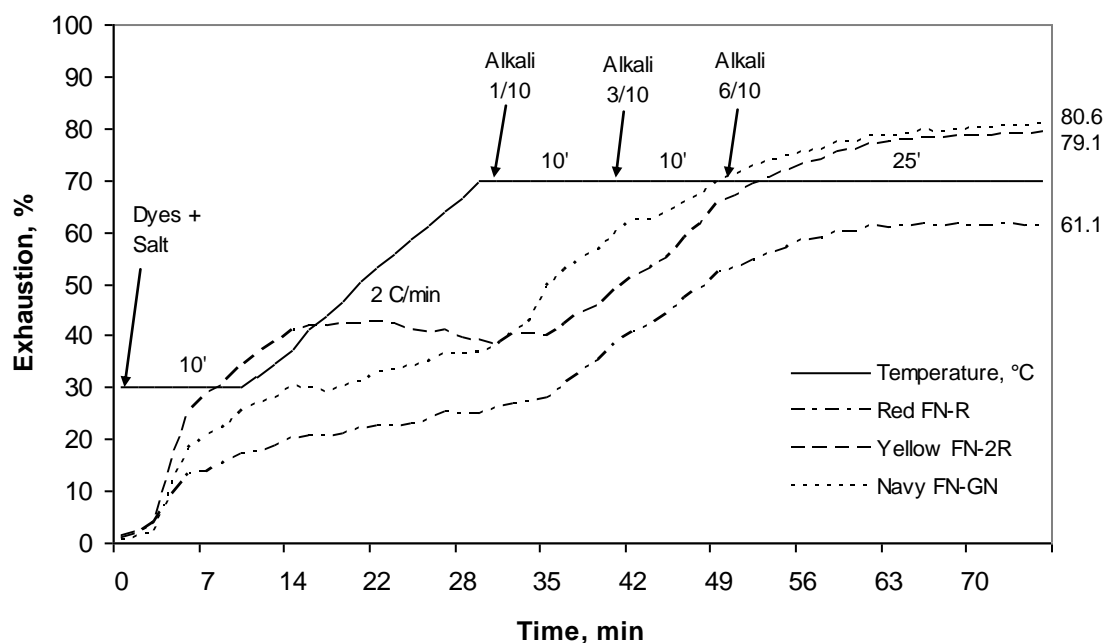


**Figure 4.7 :** The effect of alkali addition in three portions after heating up (50°C).

When the alkali addition steps were moved to fixation temperature, the rate and level of dye uptake for Novacron Red FN-R and Novacron Navy FN-GN significantly influenced. The results for Novacron Yellow FN-2R showed the same levels like previous results. It apparent that, when the temperature was increased, the exhaustion values of all dyes decreased exception of Novacron Navy FN-GN. In addition, Novacron FN-GN showed the better improvement.



**Figure 4.8 :** The effect of alkali addition in three portions after heating up (60°C).



**Figure 4.9 :** The effect of alkali addition in three portions after heating up (70°C).

The results obtained for the colorimetric values of dyed fabric are summarised in Table 4.1. Generally, portionwise addition of alkali gave the better results exception of high temperature. The result indicates that 60°C is a suitable temperature for all three dyes used in dyebath. If the temperature is bigger than 60°C, the hydrolysis of the dyes takes place, which results in a decrease in the dye-uptake. Furthermore, addition of alkali at the fixation temperature improved the dyeing performance of all dyes. We will carry on with portionwise addition alkali at 60°C.

**Table 4.1 :** Colorimetric values of dyed fabric.

| Preliminary Dyeing Experiments                             | L*    | a*   | b*    | K/S   |
|--|-------|------|-------|-------|
| Alkali addition in one portion before heating up (50°C)    | 31.66 | 8.30 | 10.93 | 11.02 |
| Alkali addition in one portion before heating up (60°C)    | 31.38 | 7.38 | 11.21 | 11.47 |
| Alkali addition in one portion before heating up (70°C)    | 32.17 | 6.69 | 11.59 | 10.95 |
| Alkali addition in three portions before heating up (50°C) | 30.06 | 8.32 | 10.26 | 12.02 |
| Alkali addition in three portions before heating up (60°C) | 30.24 | 7.47 | 10.56 | 12.04 |
| Alkali addition in three portions before heating up (70°C) | 30.51 | 7.03 | 10.92 | 12.10 |
| Alkali addition in three portions after heating up (50°C)  | 29.16 | 7.72 | 8.61  | 11.96 |
| Alkali addition in three portions after heating up (60°C)  | 29.06 | 6.62 | 8.5   | 12.16 |
| Alkali addition in three portions after heating up (70°C)  | 30.94 | 5.41 | 9.11  | 10.70 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.2.

**Table 4.2 :** Color fastness results of dyeings with different alkali addition and temperature.

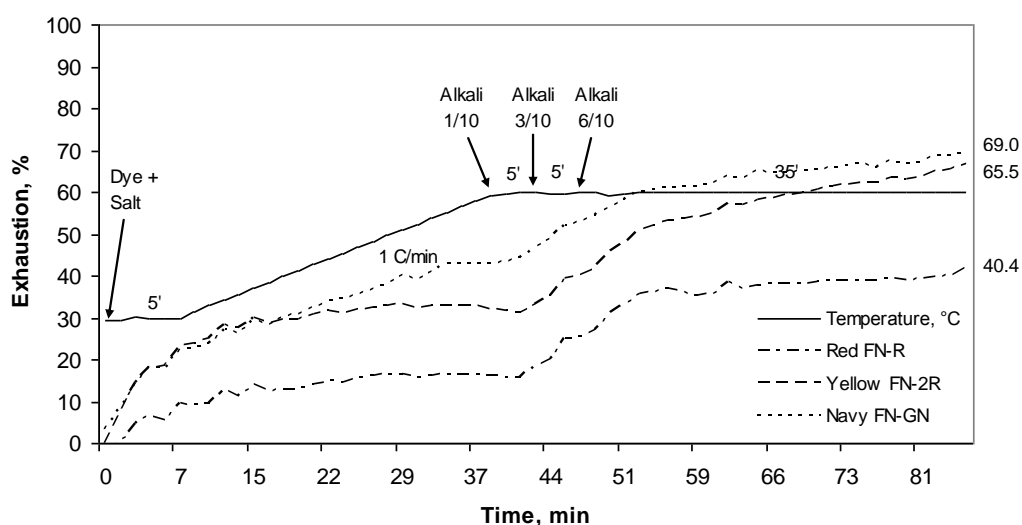
| Dyeings  | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|--|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|  | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| Alkali addition in one portion before heating up (50°C)    | 5                | 4/5          | 3/4            | 4/5          | 3                            | 4            | 2/3                              | 5            | 4/5              | 2/3 | 2              |
| Alkali addition in one portion before heating up (60°C)    | 5                | 4/5          | 3/4            | 4/5          | 3                            | 4/5          | 2/3                              | 4            | 4/5              | 3   | 2              |
| Alkali addition in one portion before heating up (70°C)    | 5                | 4            | 4              | 4/5          | 3                            | 4            | 3                                | 4            | 4/5              | 2   | 2              |
| Alkali addition in three portions before heating up (50°C) | 5                | 4/5          | 3/4            | 4/5          | 3                            | 4/5          | 2/3                              | 4            | 4/5              | 2   | 2              |
| Alkali addition in three portions before heating up (60°C) | 4/5              | 4/5          | 3/4            | 4/5          | 3                            | 4            | 2/3                              | 5            | 4/5              | 2/3 | 2              |
| Alkali addition in three portions before heating up (70°C) | 5                | 4/5          | 3/4            | 4/5          | 3                            | 4/5          | 2/3                              | 4/5          | 4/5              | 2   | 2              |
| Alkali addition in three portions after heating up (50°C)  | 5                | 4/5          | 4              | 4/5          | 3                            | 5            | 3                                | 4/5          | 4/5              | 2/3 | 2              |
| Alkali addition in three portions after heating up (60°C)  | 5                | 5            | 4              | 4/5          | 3/4                          | 4/5          | 3                                | 4/5          | 4/5              | 2/3 | 2              |
| Alkali addition in three portions after heating up (70°C)  | 5                | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 5            | 4/5              | 2/3 | 2              |

Changing the steps of alkali addition and fixation temperature did not have any particular affect on the fastness properties.

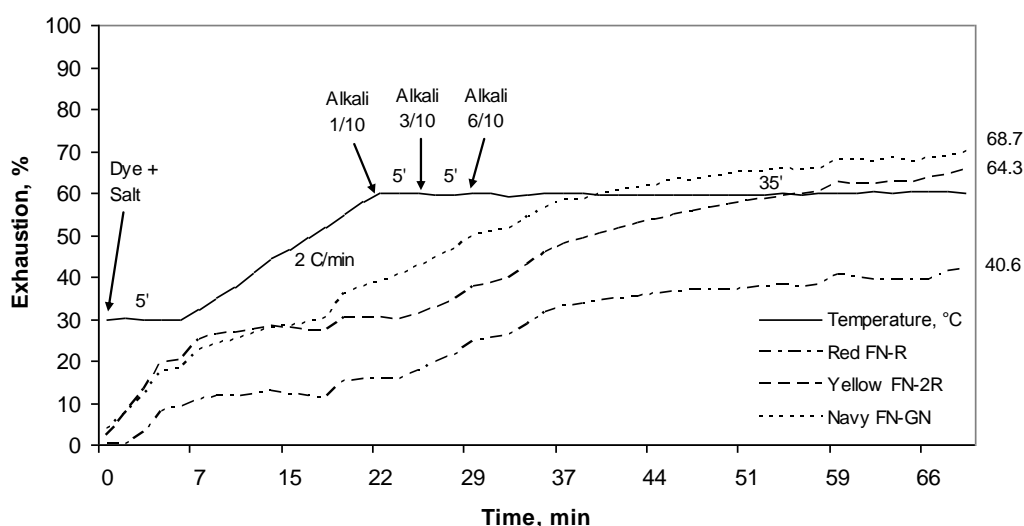
#### 4.1.2 Effect of temperature gradient

In order to investigate the effect of temperature gradient in dyeing procedure, we conducted trials with 1 and 2°C/min.

The following dyeings were performed at a liquor ratio of 50:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were 60 g/L sodium sulfate and 10 g/L sodium carbonate. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

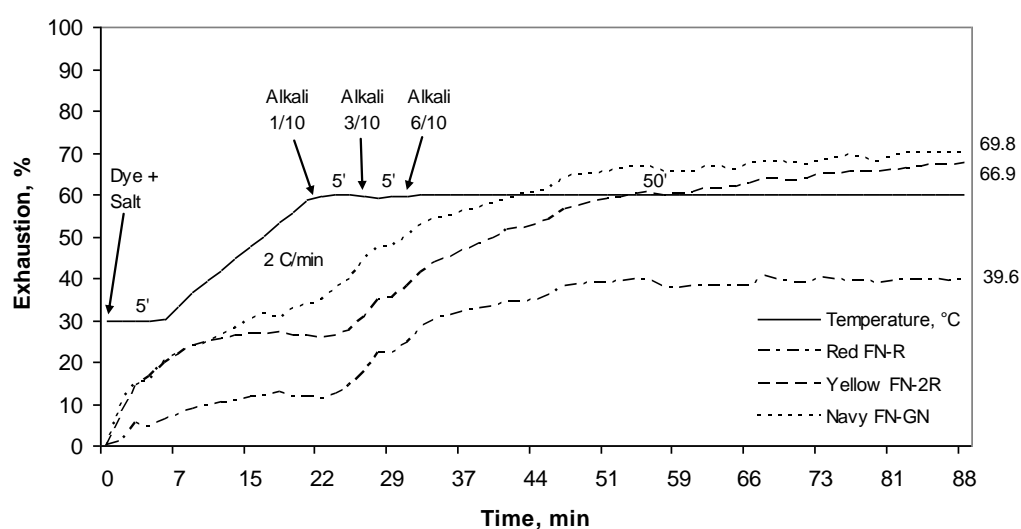


**Figure 4.10 :** The effect of 1°C/min temperature gradient on exhaustion profiles.



**Figure 4.11 :** The effect of 2°C/min temperature gradient on exhaustion profiles.

When the Figures 4.10 and 4.11 are compared, it is seen that there is no big difference in final exhaustion values for both dyeings. We will carry on with 2°C/min as temperature gradient. Because, when 2°C/min is used instead of 1°C/min, the total dyeing time will reduce in 15 min. It is observed that exhaustion values of all three dyes still continue to increase at the end of dyeing. It can be inferred that the waiting time at the fixation temperature was not enough for complete exhaustion. For this reason, another trial was performed to see the effect of longer waiting time on exhaustion values. The waiting time at the fixation temperature was increased from 45 to 60 min, whereas all other dyeing parameters were kept same.



**Figure 4.12 :** The effect of longer waiting time at fixation temperature on exhaustion profiles.

It is apparent from Figure 4.12 that the longer waiting time did not affect the exhaustion value of Novacron Red FN-R positively, but increased the exhaustion values of Novacron Yellow FN-2R and Novacron Navy FN-GN. These improvements were not good as expected, for that reason the longer waiting time was not preferred for the following trials.

The fixation and color strength results are as shown in Table 4.3. It is apparent that both fixation and color strength values are not that different for all dyeings, but longer waiting time affected fixation value of Novacron FN-R negatively. These results are in accordance with exhaustion results.



**Table 4.3 :** Effect of temperature gradient on fixation and color strength values.

| Temperature gradient, °C/min | Fixation, % |              |            | K/S  |
|------------------------------|-------------|--------------|------------|------|
|                              | Red FN-R    | Yellow FN-2R | Navy FN-GN |      |
| 1                            | 68.63       | 88.03        | 90.58      | 8.47 |
| 2                            | 68.95       | 86.72        | 89.94      | 8.25 |
| 2<br>(longer waiting time)   | 66.79       | 88.55        | 90.70      | 8.60 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.4.

**Table 4.4 :** Color fastness results of dyeings with different temperature gradient.

| Temperature gradient, °C/min | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|------------------------------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|                              | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 1                            | 4/5              | 4/5          | 4/5            | 5            | 3/4                          | 5            | 3/4                              | 4/5          | 4/5              | 4/5 | 2/3            |
| 2                            | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 5            | 3/4                              | 4/5          | 4/5              | 4/5 | 2/3            |
| 2<br>(longer waiting time)   | 5                | 4/5          | 4/5            | 5            | 3/4                          | 4/5          | 3/4                              | 4/5          | 4/5              | 4   | 2/3            |

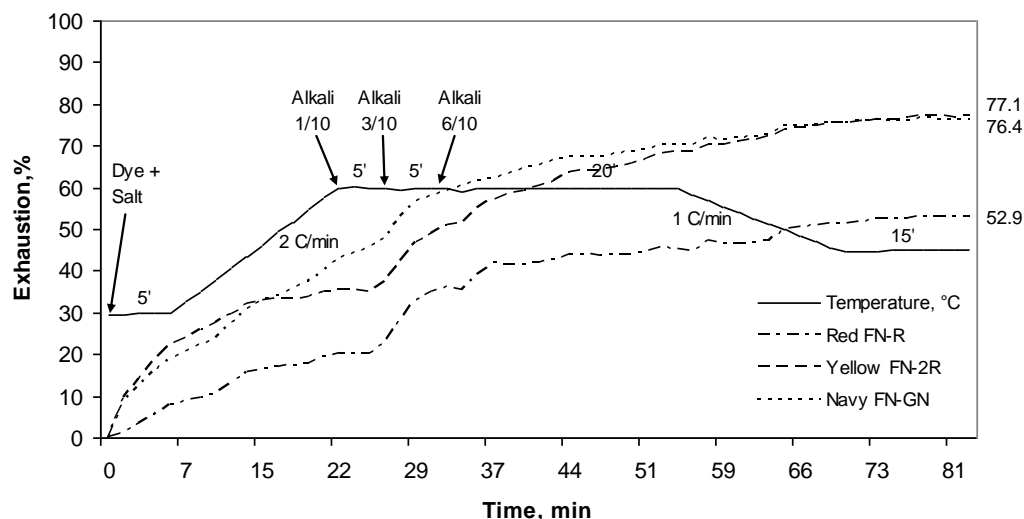
Changing the temperature gradient did not have any significant affect on the fastness properties.

#### 4.1.3 Effect of cooling step

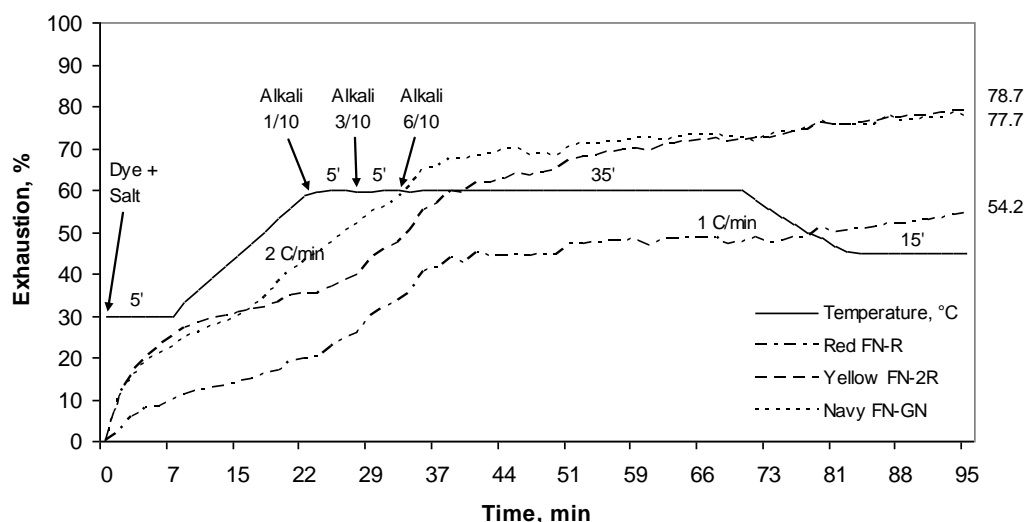
In order to investigate the effect of cooling step at the end of dyeing procedure, we conducted trials with two different waiting time.

The following dyeings were performed at a liquor ratio of 50:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were 80 g/L sodium sulfate and 20 g/L sodium carbonate. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

The cooling step is the last section of the dyeing procedure. It can be thought that the termination of dyeing without cooling step is not allowed to continue the chemical reaction between fiber and dye.



**Figure 4.13 :** The effect of cooling step at the end of dyeing.



**Figure 4.14 :** The effect of cooling step at the end of dyeing with longer waiting time.

As can be seen in Figures 4.13 and 4.14, during the cooling step, the exhaustion levels of all dyes raise apart from the waiting time. The drain of the dyebath at high temperature is demanded because of the ecological concerns. This is the another advantage of the cooling step. Because of the minor differences in exhaustion and fixation values, shorter waiting time was preferred for following dyeings.

The fixation and color strength results are as shown in Table 4.5. It was found that both fixation and color strength values are not that different for two dyeings.

results.

**Table 4.5 :** Effect of cooling step on fixation and color strength values.

| Waiting time,<br>min | Fixation, % |              |            | K/S  |
|----------------------|-------------|--------------|------------|------|
|                      | Red FN-R    | Yellow FN-2R | Navy FN-GN |      |
| 30                   | 59.98       | 84.01        | 84.17      | 9.01 |
| 45                   | 60.82       | 85.00        | 84.93      | 9.14 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.6.

**Table 4.6 :** Color fastness results of dyeings with cooling step.

| Waiting time,<br>min | Washing<br>Fastness |                 | Water<br>Fastness |                 | Perspiration<br>Fastness<br>(Acid) |                 | Perspiration<br>Fastness<br>(Alkaline) |                 | Rubbing<br>Fastness |     | Light<br>Fastness |
|----------------------|---------------------|-----------------|-------------------|-----------------|------------------------------------|-----------------|--|-----------------|---------------------|-----|-------------------|
|                      | Staining            | Color<br>Change | Staining          | Color<br>Change | Staining                           | Color<br>Change | Staining                               | Color<br>Change | Dry                 | Wet |                   |
| 30                   | 4/5                 | 4/5             | 4                 | 5               | 3                                  | 4/5             | 3                                      | 4/5             | 4/5                 | 4   | 2/3               |
| 45                   | 5                   | 4/5             | 4                 | 4/5             | 3                                  | 4               | 3                                      | 4/5             | 4/5                 | 4   | 2/3               |

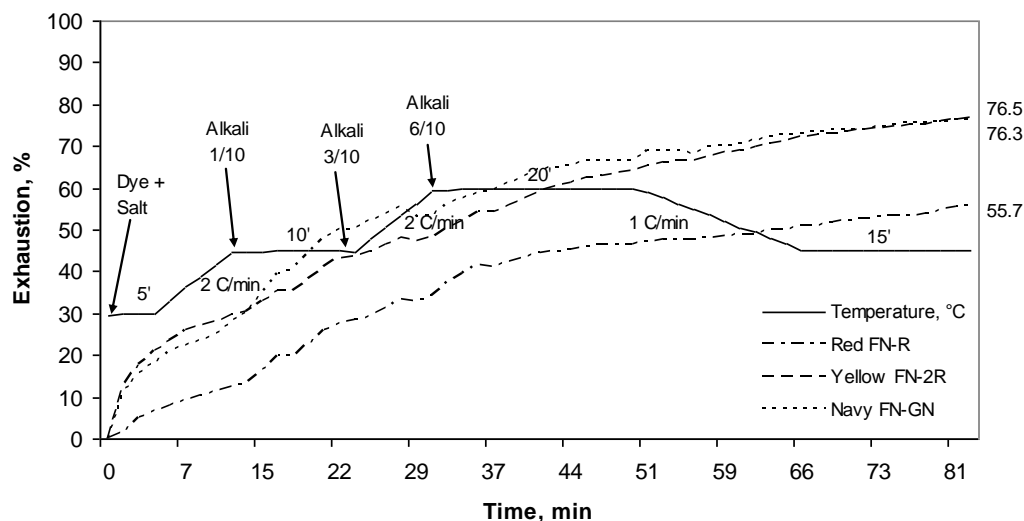
Adding the cooling step at the end of dyeing did not have any important affect on the fastness properties.

#### 4.1.4 Preliminary experiment to obtain the optimized dyeing procedure

In order to obtain optimum conditions for dyeing cotton fibers with reactive dyes, The dyeing procedure was modified it is necessary to find out how dyeing results depend on the addition of auxiliaries are

Exhaustion curves of previous experiments may not be preferable in terms of dyeing levelness. Therefore, it was decided to modify dyeing procedues as shown in Figure 4.13. Instead of adding alkali at the fixation temperature, first two portions of the alkali were added to the dyebath while temperature was increasing. All other dyeing parameters were kept same. The modified dyeing procedure is presented in Figure 4.15. When the modified and previous procedures were compared, the final

exhaustion values of Novacron Yellow FN-2R and Novacron Navy FN-GN for both procedure were almost same whereas the exhaustion value of Novacron Red FN-R was higher.



**Figure 4.15 :** The exhaustion profiles of modified dyeing procedure.

The fixation and color strength results of modified dyeing procedure are shown in Table 4.7. The modified procedure gave higher fixation and K/S values as compared to previous procedure (see Table 4.3).

**Table 4.7 :** Fixation and color strength results of modified dyeing procedure.

| Fixation, % |              |            | K/S  |
|-------------|--------------|------------|------|
| Red FN-R    | Yellow FN-2R | Navy FN-GN |      |
| 70.15       | 85.55        | 86.76      | 9.33 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.8.

**Table 4.8 :** Color fastness results of dyeings with modified procedure.

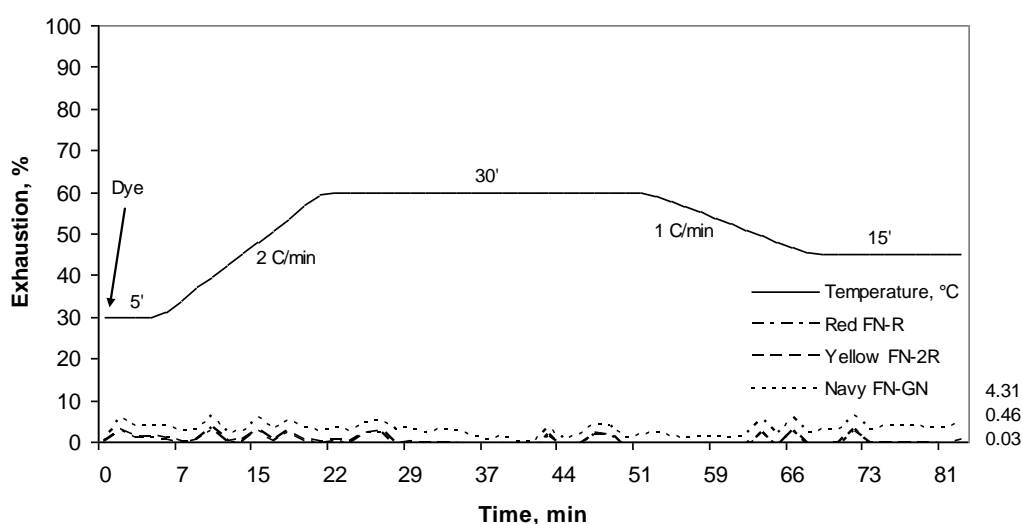
| Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
| Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 5                | 4            | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 4/5              | 3/4 | 2/3            |

Changing the dyeing procedure did not improve the fastness properties in comparison with previous procedures.

#### 4.1.5 Effect of electrolyte and alkali

In order to obtain optimum conditions for dyeing cotton fibers with reactive dyes, it is necessary to find out how dyeing results depend on the addition of auxiliaries are important. The most important auxiliaries in reactive dyeing are electrolyte and alkali. In order to investigate the effect of electrolyte and alkali, we conducted a series of dyeing. The procedure used for the dyeing experiments was described previously. The amounts of electrolyte and alkali were varied.

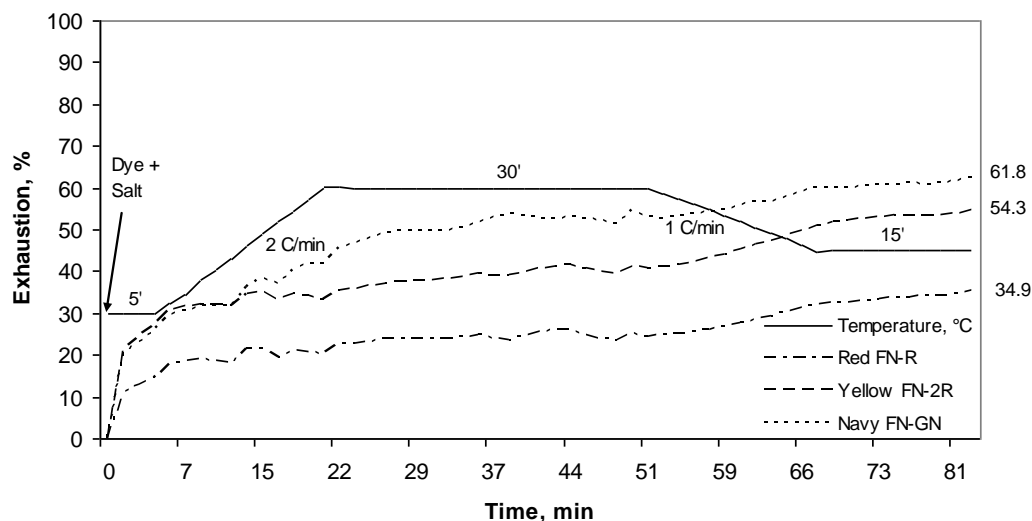
The following dyeings were performed at a liquor ratio of 50:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were sodium sulfate and sodium carbonate. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.



**Figure 4.16 :** The exhaustion profiles of dyeing with no electrolyte and alkali.

In the first dyeing experiment, electrolyte and alkali were not added to dyebath. When there was no electrolyte and alkali in the dyebath, almost all dyes came off (see Figure 4.16). In other words, the dye uptake from dyebath to fiber did not happen.

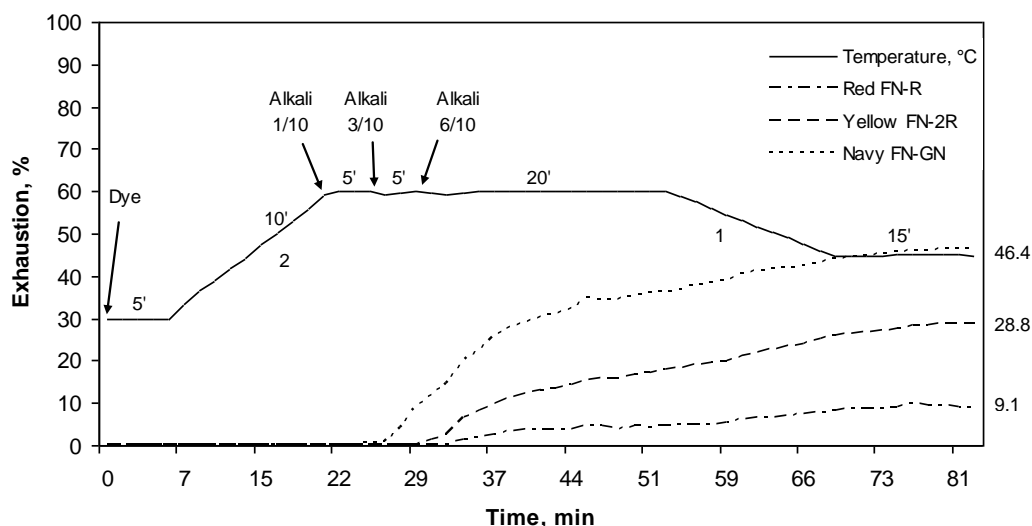
In the second dyeing experiment, 70 g/L electrolyte was added to dyebath without alkali to investigate the individual effect of electrolyte. As can be seen in Figure 4.17, the presence of electrolyte in dyebath drastically affected the exhaustion levels of all dyes when compared with Figure 4.16. It is very important to understand the role of electrolyte in dyeing mechanism. Besides, Novacron Red FN-R was not affected by addition of alkali as much as other two dyes.



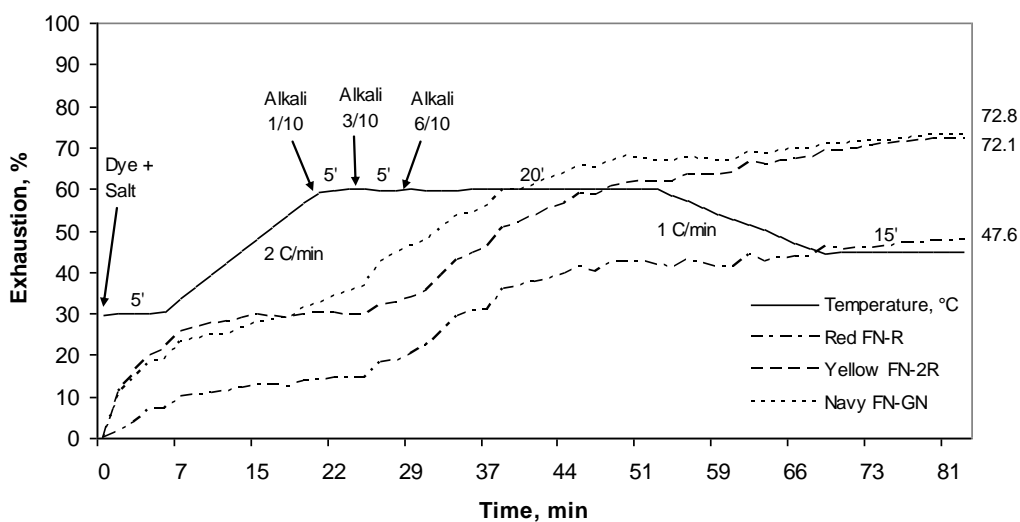
**Figure 4.17 :** The exhaustion profiles of dyeing used 70 g/L electrolyte and no alkali.

In the next dyeing experiment, 15 g/L alkali was added to dyebath without electrolyte to investigate the individual effect of alkali. Figure 4.18 showed that when no alkali was present in the dyebath during the preliminary exhaustion stage, the exhaustion did not appear. The exhaustion occurred after the addition of alkali. Also, the effect of electrolyte on exhaustion was stronger than the effect of alkali on exhaustion.

Another dyeing experiment was conducted to investigate the exhaustion profiles when the electrolyte and alkali were used together. The exhaustion profiles of all three dyes are shown in Figure 4.19. The shape of exhaustion curves showed that a great effect of using electrolyte and alkali together at certain concentration led to an important increase in exhaustion values.



**Figure 4.18 :** The exhaustion profiles of dyeing used 15 g/L alkali and no electrolyte.



**Figure 4.19 :** The exhaustion profiles of dyeing used 70 g/L electrolyte and 15 g/L alkali.

The fixation and color strength results are as shown in Table 4.9. It was found that there was no fixation at the zero levels of electrolyte and alkali. When the electrolyte was used alone as auxiliaries, it improved the all fixation and color strength results. When the alkali was used alone as auxiliaries, the better results were achieved comparing to where electrolyte was used alone. The highest fixation and color strength results are achieved when the electrolyte and alkali are used together.

**Table 4.9 :** Effect of electrolyte and alkali on fixation and color strength values.

| Dyeing                               | Fixation, % |              |            | K/S  |
|--------------------------------------|-------------|--------------|------------|------|
|                                      | Red FN-R    | Yellow FN-2R | Navy FN-GN |      |
| No electrolyte and alkali            | N/A         | N/A          | N/A        | 0.15 |
| 70 g/L electrolyte and no alkali     | 1.94        | 18,76        | 34.75      | 1.71 |
| No electrolyte and 15 g/L alkali     | N/A         | 60.35        | 78.56      | 3.13 |
| 70 g/L electrolyte and 15 g/L alkali | 65.96       | 84.53        | 87.18      | 8.70 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.10.

**Table 4.10 :** Color fastness results of dyeings with or without electrolyte and alkali.

| Dyeing                               | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|--------------------------------------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|                                      | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| No electrolyte and alkali            | 5                | 3/4          | 4/5            | 4            | 4/5                          | 4/5          | 4/5                              | 4            | 4/5              | 4/5 | 2              |
| 70 g/L electrolyte and no alkali     | 4/5              | 4            | 3/4            | 4            | 4/5                          | 4            | 4/5                              | 4/5          | 4/5              | 4/5 | 2/3            |
| No electrolyte and 15 g/L alkali     | 4                | 4/5          | 4/5            | 4/5          | 4/5                          | 4/5          | 4/5                              | 4/5          | 4/5              | 4   | 3              |
| 70 g/L electrolyte and 15 g/L alkali | 4/5              | 4            | 4/5            | 5            | 3/4                          | 4/5          | 3/4                              | 4/5          | 4/5              | 3/4 | 2/3            |

The presence of electrolyte and alkali did not have an significant affect on the fastness properties.

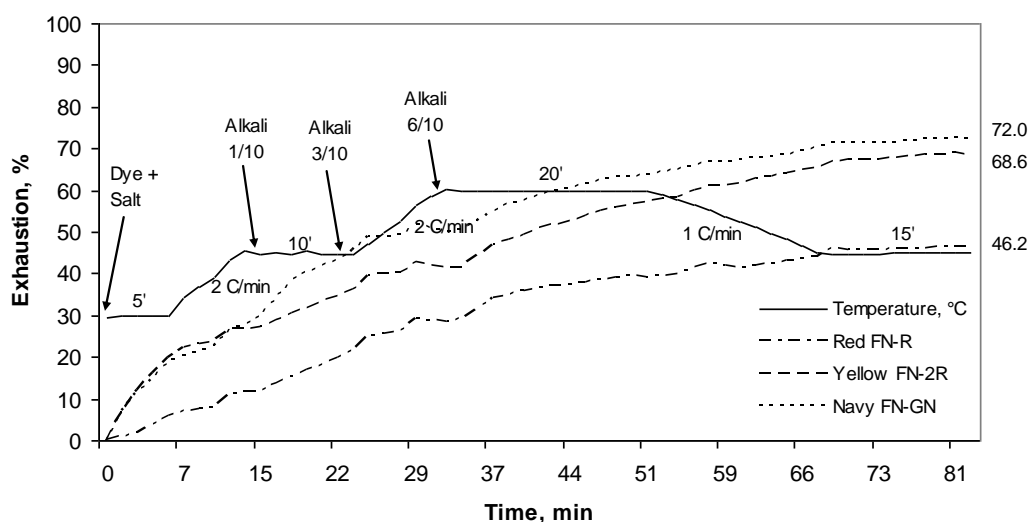
#### 4.1.6 Effect of concentrations of electrolyte and alkali

In order to investigate the effect electrolyte and alkali concentrations, we conducted trials with different electrolyte and alkali concentrations. The aim of these trials was to determine the base levels for central composite design.



The modified dyeing procedure where the first two portions of alkali were added during the heating up was used for the following dyeings. All dyeings were performed at a liquor ratio of 50:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. The amounts of electrolyte and alkali used were namely 60-10, 70-15, 80-20, 90-25 and 100-30 g/L. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

The results of the dyebath exhaustion analysis for the samples dyed with the five different levels of auxiliaries are presented in Figure 4.20-4.24.

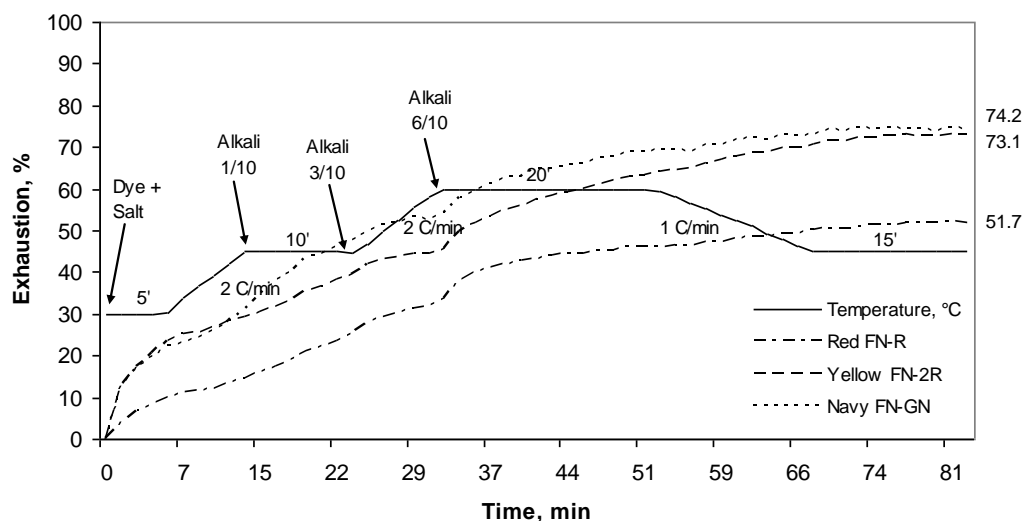


**Figure 4.20 :** The exhaustion curves for dyeing used 60 g/L electrolyte and 10 g/L alkali.

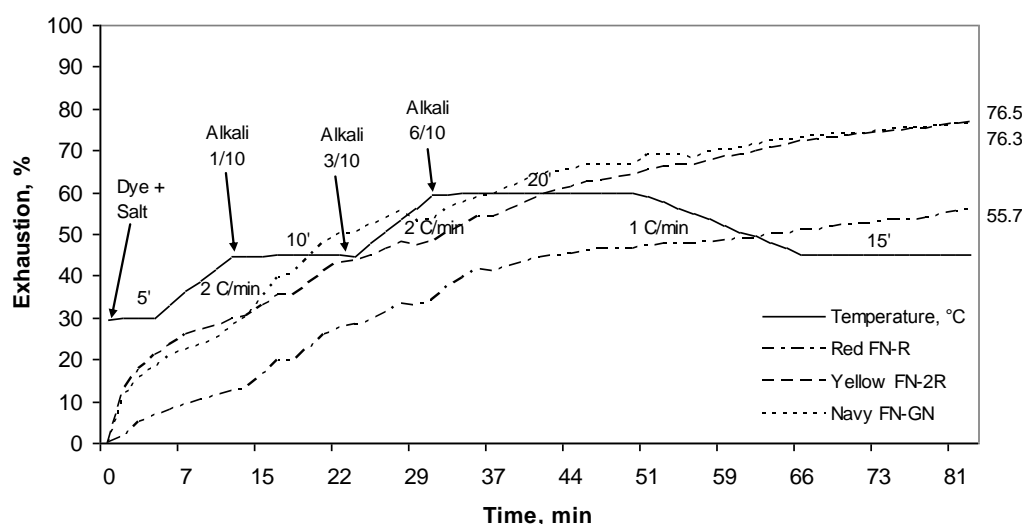
In the first trial, the amounts of electrolyte and alkali were chosen 60 and 10 g/L respectively (see Figure 4.20). Actually, these levels of auxiliaries are not enough for this dye concentration and recommended by dye manufacturers, but it was aimed to examine the dyeing performance at low levels of auxiliaries. The final dyebath exhaustion was significantly low.

As seen from Figure 4.21 and 4.22, increase in auxiliary levels led to increase in dyebath exhaustion for the three dyes. The exhaustion of reactive dyes by the cellulosic fibers can be divided into two distinct phases. In the primary exhaustion stage, where no reaction occurs between the dye and the fiber, mobility of the dye

within the dyebath-fiber media is restricted only by its affinity for this phase. Electrolyte may be the one of the most important factors affecting the dye uptake behaviour. During the secondary exhaustion stage, when the temperature is increased and the reaction between the dye and fiber takes place.



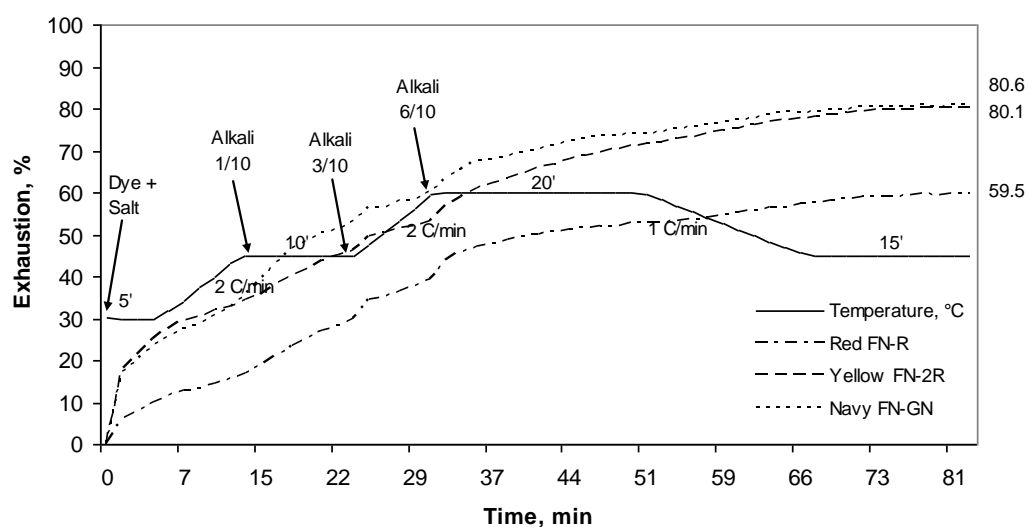
**Figure 4.21 :** The exhaustion curves for dyeing used 70 g/L electrolyte and 15 g/L alkali.



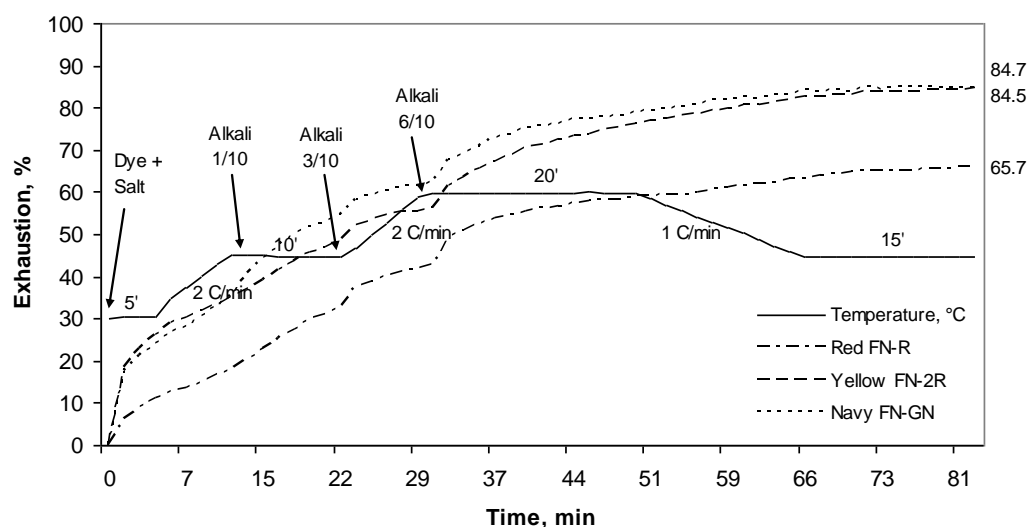
**Figure 4.22 :** The exhaustion curves for dyeing used 80 g/L electrolyte and 20 g/L alkali.

It is clear from Figures 4.23 and 4.24 that when the auxiliary levels are increased, the exhaustion values increased. Normally, using these amounts of auxiliaries in dyeing process is an undesired situation as it gives rise to some ecological problems. The

purpose of these dyeings was to investigate the dyeing performance at high levels of auxiliaries.



**Figure 4.23 :** The exhaustion curves for dyeing used 90 g/L electrolyte and 25 g/L alkali.



**Figure 4.24 :** The exhaustion curves for dyeing with 100 g/L electrolyte and 30 g/L alkali.

The fixation and color strength results are as shown in Table 4.11. It was found that the highest fixation values for all three dyes were achieved, when the amounts of electrolyte and alkali were 70 g/L and 15 g/L respectively. The color strength values were parallel with the fixation values. When the levels of auxiliaries were moved over the 80-20 g/L level, the fixation values started to decrease.

**Table 4.11 :** Effect of concentrations of electrolyte and alkali on fixation and color strength values.

| Dyeing                                | Fixation, % |              |            | K/S  |
|---------------------------------------|-------------|--------------|------------|------|
|                                       | Red FN-R    | Yellow FN-2R | Navy FN-GN |      |
| 60 g/L electrolyte and 10 g/L alkali  | 67.86       | 82.71        | 84.51      | 8.63 |
| 70 g/L electrolyte and 15 g/L alkali  | 69.33       | 86.70        | 88.50      | 9.51 |
| 80 g/L electrolyte and 20 g/L alkali  | 70.15       | 85.55        | 86.76      | 9.33 |
| 90 g/L electrolyte and 25 g/L alkali  | 67.18       | 84.72        | 86.49      | 9.21 |
| 100 g/L electrolyte and 30 g/L alkali | 68.51       | 83.34        | 87.39      | 9.14 |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.12.

**Table 4.12 :** Color fastness results of dyeings with different levels of electrolyte and alkali.

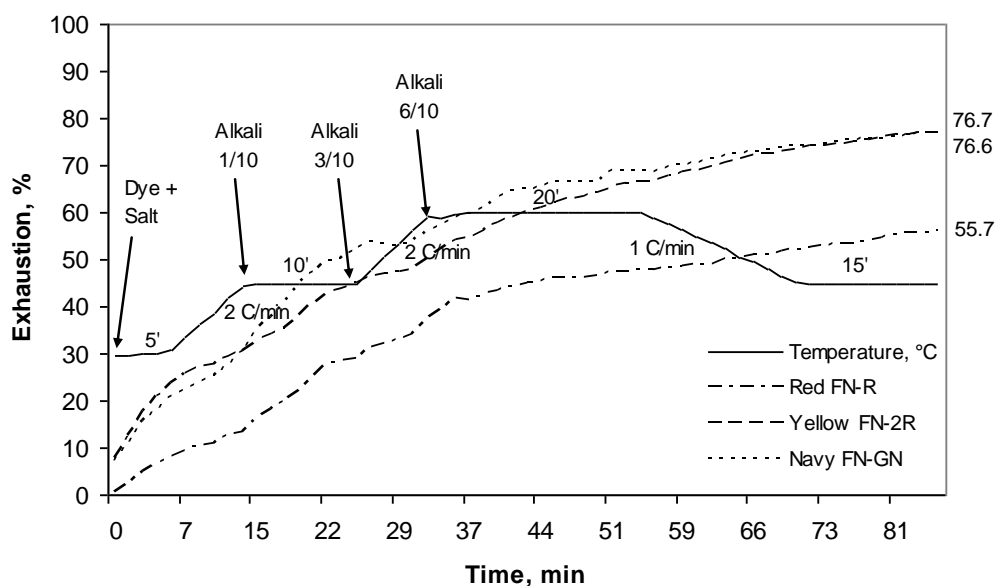
| Dyeing                                | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|---------------------------------------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|                                       | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 60 g/L electrolyte and 10 g/L alkali  | 5                | 4/5          | 4              | 4/5          | 3/4                          | 4/5          | 3/4                              | 4/5          | 4/5              | 4   | 2/3            |
| 70 g/L electrolyte and 15 g/L alkali  | 4/5              | 4/5          | 4              | 4/5          | 3/4                          | 4/5          | 3                                | 4/5          | 4/5              | 3/4 | 2              |
| 80 g/L electrolyte and 20 g/L alkali  | 5                | 4            | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 4/5              | 3/4 | 2/3            |
| 90 g/L electrolyte and 25 g/L alkali  | 4                | 4/5          | 3/4            | 4/5          | 3                            | 4/5          | 3                                | 5            | 4/5              | 3/4 | 2              |
| 100 g/L electrolyte and 30 g/L alkali | 3                | 4/5          | 3/4            | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 4/5              | 3   | 2              |

The results indicated that when the levels of auxiliaries are increased, the staining results of washing fastness decreased. This is due to dye hydrolysis at high alkali concentration. The other fastness properties were not affected by changes in the concentrations of electrolyte and alkali.

#### 4.1.7 Effect of liquor to goods ratio

The range of liquor to goods ratios (L:R) employed varied from 50:1 to 30:1, 25:1, 20:1 and finally 15:1 to explore the effect of variations in liquor to goods ratio on exhaustion and fixation profiles of individual dyes in a dyeing recipe.

Figure 4.25 shows the exhaustion profile of all three dyes used separately at a liquor to goods ratio of 50:1.

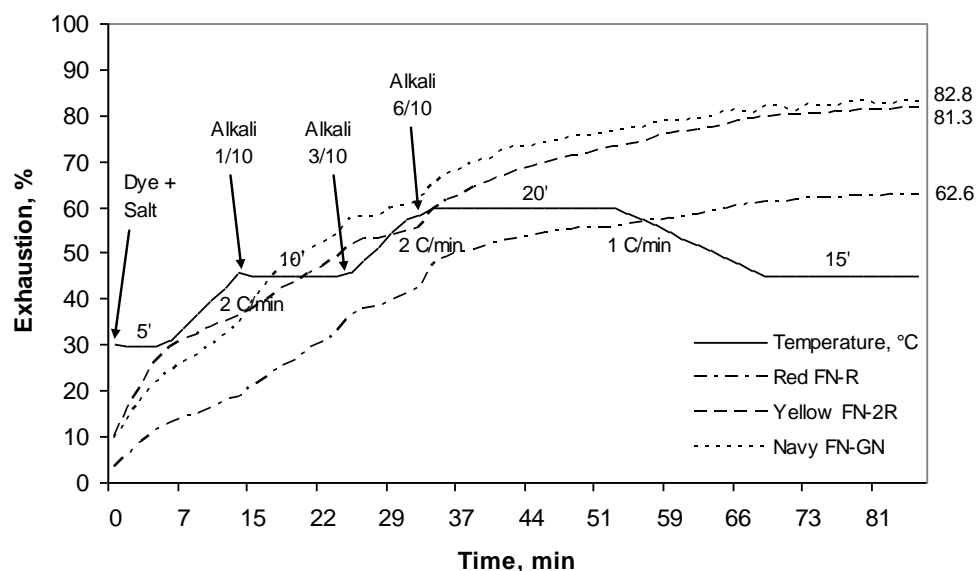


**Figure 4.25 :** The effect of 50:1 liquor to goods ratio on exhaustion profiles.

Although generally reactive dyes exhibit high exhaustion values, under appropriate application conditions, it can be seen that at a L:R of 50:1 the three dyes employed in this study, especially Novacron Red FN-R, exhibited relatively low exhaustion values which was likely due to the high liquor to goods ratio employed. In addition, it is apparent that the exhaustion performance of Novacron Red FN-R was apparently weaker than the other two dyes during the entire dyeing process. Such low levels of dye exhaustion would not be economically or indeed ecologically acceptable since the remaining dye in the dyebath requires wastewater treatment and is a source of pollution. Figure 4.26 shows the exhaustion profiles of the three reactive dyes at liquor to goods ratio of 30:1.

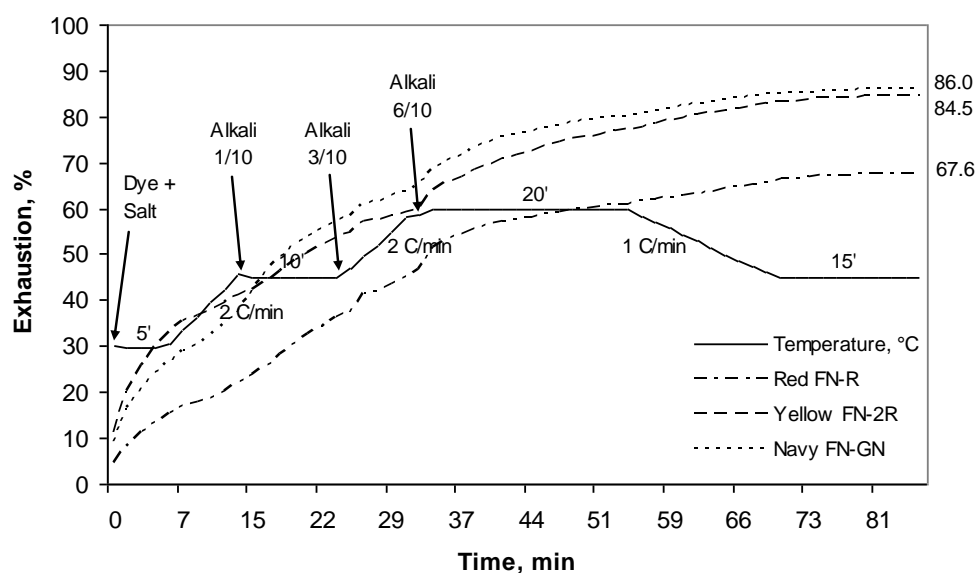
While the overall shape of exhaustion curves shown in Figure 4.26 appear to follow those shown in Figure 4.25, it can be seen that a decrease in liquor to goods ratio from 50:1 to 30:1 has significantly influenced the rate and level of dye uptake during

the dyeing process. Indeed the overall exhaustion values of all dyes are increased; the biggest shift of %11 being observed for Novacron Red FN-R. However, it can also be seen that the difference in exhaustion rate of Novacron Red FN-R and other dyes was still high.

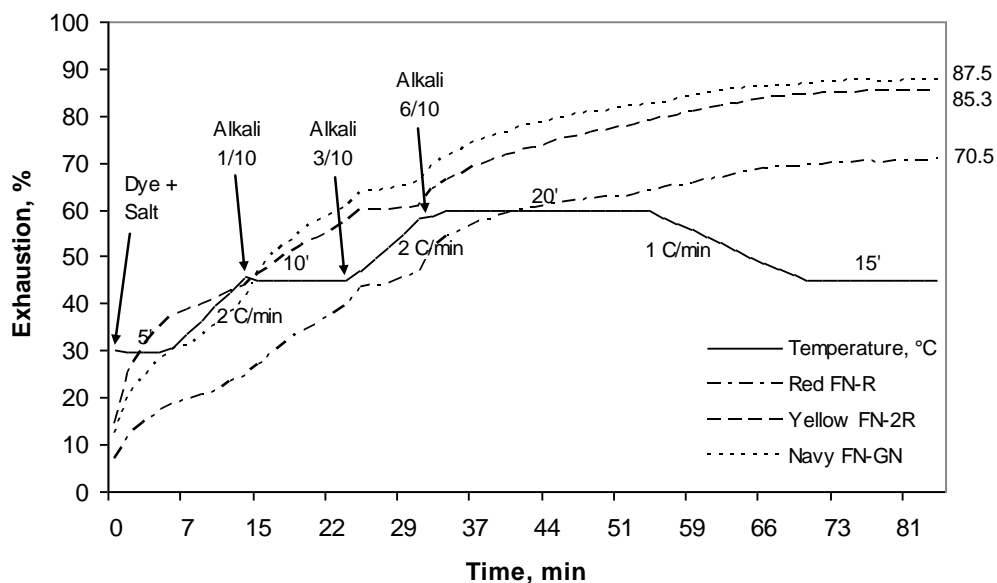


**Figure 4.26 :** The effect of 30:1 liquor to goods ratio on exhaustion profiles.

Figure 4.27 and 4.28 show the exhaustion profiles of dyes at 25:1 and 20:1 liquor to goods ratios respectively.

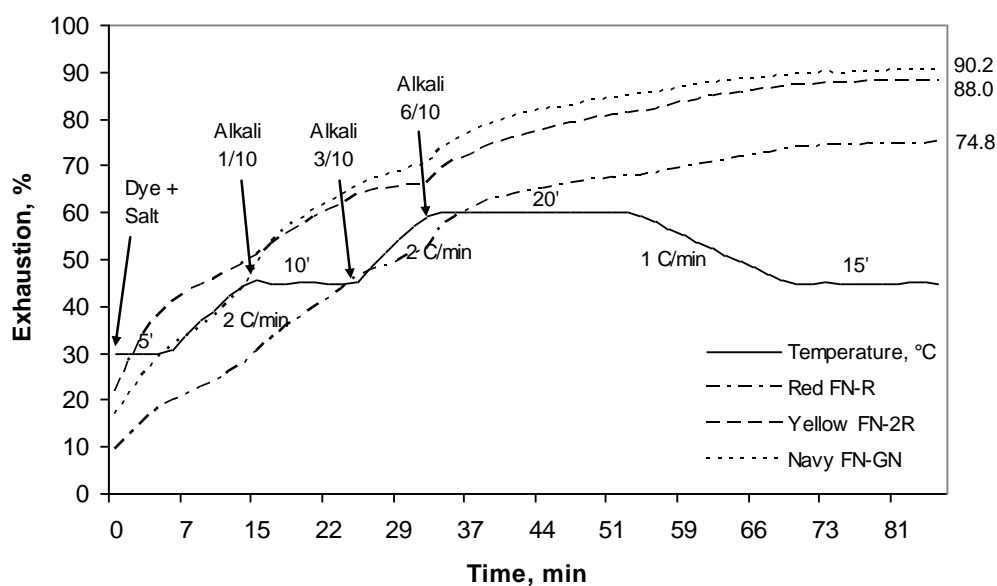


**Figure 4.27 :** The effect of 25:1 liquor to goods ratio on exhaustion profiles.



**Figure 4.28 :** The effect of 20:1 liquor to goods ratio on exhaustion profiles.

The application of lower liquor to goods ratios favors dye absorption which provides an increased opportunity for the dye molecule to react with the fiber. It is apparent from Figure 4.27 and 4.28 that decreasing the liquor to goods ratio has further influenced the balance between dye absorption and desorption. Moreover, the exhaustion curves seem to approach equilibrium unlike those shown at higher liquor to goods ratios.



**Figure 4.29 :** The effect of 15:1 liquor to goods ratio on exhaustion profiles.

Figure 4.29 shows the exhaustion values for three dyes employed at a liquor to goods ratio of 15:1. In the case of Novacron Yellow FN-2R and Novacron Navy FN-GN dyes the overall exhaustion values seem to have reached the maximum levels while the overall exhaustion of Novacron Red FN-R has not reached the same levels. Indeed when the liquor to goods ratio was decreased from 50:1 to 15:1 the difference in the final exhaustion level of Novacron Red FN-R and that of Novacron Yellow FN-2R and Novacron Navy FN-GN dyes drops from approximately 21% to approximately 13%.

While the reduction in liquor to goods ratio has improved the performance of Novacron Red FN-R in this commercially recommended trichromatic set, it is shown that this dye is probably an unsuitable candidate for the generation of colors based on a trichromatic mixture. However, it can also be seen that while all other dyeing conditions were kept identical during the dyeing process, the overall exhaustion level of this dye was significantly increased by adjusting the liquor to goods ratio in the dyebath. Although a liquor to goods ratio of 15:1 may be considered more practical in an industrial setting, color matching of samples in a laboratory setting may involve application of dyes at higher liquor to goods ratios.

Results demonstrated that variability in performance of individual dyes in admixture, as a result of variations in liquor to goods ratio, would result in significant variations in the final shades of dyed samples. This could have a significant impact on lab to bulk productions with subsequent impacts on achieving right-every-time philosophy. started to decrease.

**Table 4.13 :** Effect of liquor to goods ratio on fixation and color strength values.

| Liquor to goods<br>ratio | Fixation, % |              |            | K/S   |
|--------------------------|-------------|--------------|------------|-------|
|                          | Red FN-R    | Yellow FN-2R | Navy FN-GN |       |
| 50:1                     | 70.15       | 85.55        | 86.76      | 9.33  |
| 30:1                     | 71.58       | 85.69        | 88.56      | 10.01 |
| 25:1                     | 72.16       | 85.93        | 89.22      | 10.72 |
| 20:1                     | 71.37       | 82.26        | 86.13      | 9.96  |
| 15:1                     | 70.71       | 81.99        | 85.03      | 10.17 |



Table 4.13 shows the effect of variations in liquor to goods ratio on fixation and color strength values of dyes used in a trichromatic recipe. Normally, as the liquor to goods ratio decreases the fixation values are expected to increase because decreased liquor to goods ratio increases the possibility of covalent bond formation between the dye and fiber.

Results obtained in these trials show that while a general decrease in the liquor to goods ratio from 50:1 to 25:1 results in increasing the fixation values for all dyes on cotton fiber, this trend does not continue beyond that point. Indeed a further reduction in liquor to goods ratio from 25:1 to 15:1 results in an apparent reduction in fixation of all three dyes employed during this study. Once again, this demonstrates the significance of variations in liquor to goods ratio on the final shade of dyed substrates and provides insight on the potential determination of optimal liquor to goods ratio for various trichromatic sets applied to different fibers. In addition, the study shows the effectiveness of real time monitoring and data acquisition systems on generating suitable control strategies for various dye-fiber combinations. The highest K/S value is measured at liquor to goods ratio of 25:1, and the changing trend of K/S values with decreasing liquor to goods ratio is parallel with exhaustion results obtained from the monitoring system.

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.14.

**Table 4.14 :** Color fastness results of dyeings with different liquor to goods ratio.

| Liquor to goods ratio | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|-----------------------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|                       | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 50:1                  | 5                | 4            | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 4/5              | 3/4 | 2/3            |
| 30:1                  | 4/5              | 4/5          | 4              | 4/5          | 3                            | 4/5          | 3/4                              | 4/5          | 4/5              | 3/4 | 2              |
| 25:1                  | 4/5              | 4/5          | 4              | 4/5          | 3                            | 4            | 3/4                              | 4/5          | 4/5              | 3/4 | 2              |
| 20:1                  | 4                | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3/4                              | 5            | 4/5              | 4   | 2              |
| 15:1                  | 4/5              | 5            | 4/5            | 4/5          | 3                            | 4            | 3                                | 4/5          | 4/5              | 3/4 | 2              |

The results indicated that when the liquor to goods ratio are decreased, the color fastness results are not changed.

## 4.2 Results of Central Composite Designed Experiments

The following dyeings were performed at a liquor ratio of 25:1 using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were sodium sulfate and sodium carbonate.

**Table 4.15 :** Coded and actual design factor levels for optimization.

| Coded ID | Electrolyte, g/L | Alkali, g/L | Temperature, °C | Waiting time, min | Fixation, % |              |            |
|----------|------------------|-------------|-----------------|-------------------|-------------|--------------|------------|
|          |                  |             |                 |                   | Red FN-R    | Yellow FN-2R | Navy FN-GN |
| 1        | 60               | 10          | 55              | 25                | 76.02       | 85.42        | 86.54      |
| 2        | 60               | 10          | 55              | 35                | 76.52       | 85.51        | 87.55      |
| 3        | 60               | 10          | 65              | 25                | 77.13       | 87.27        | 87.05      |
| 4        | 60               | 10          | 65              | 35                | 78.15       | 87.39        | 88.09      |
| 5        | 60               | 20          | 55              | 25                | 78.29       | 88.01        | 88.02      |
| 6        | 60               | 20          | 55              | 35                | 78.18       | 89.03        | 88.41      |
| 7        | 60               | 20          | 65              | 25                | 78.27       | 89.31        | 88.72      |
| 8        | 60               | 20          | 65              | 35                | 78.69       | 89.42        | 89.02      |
| 9        | 80               | 10          | 55              | 25                | 76.78       | 85.52        | 79.05      |
| 10       | 80               | 10          | 55              | 35                | 76.97       | 85.48        | 78.94      |
| 11       | 80               | 10          | 65              | 25                | 77.44       | 87.29        | 87.05      |
| 12       | 80               | 10          | 65              | 35                | 78.33       | 87.78        | 87.23      |
| 13       | 80               | 20          | 55              | 25                | 78.67       | 88.11        | 87.02      |
| 14       | 80               | 20          | 55              | 35                | 79.17       | 88.93        | 86.92      |
| 15       | 80               | 20          | 65              | 25                | 79.47       | 90.4         | 90.2       |
| 16       | 80               | 20          | 65              | 35                | 79.98       | 90.41        | 90.02      |
| 17       | 50               | 15          | 60              | 30                | 73.24       | 88.73        | 88.33      |
| 18       | 90               | 15          | 60              | 30                | 80.23       | 89.75        | 88.35      |
| 19       | 70               | 5           | 60              | 30                | 74.07       | 84.61        | 83.86      |
| 20       | 70               | 25          | 60              | 30                | 75.07       | 84.82        | 84.89      |
| 21       | 70               | 15          | 50              | 30                | 77.75       | 87.32        | 87.61      |
| 22       | 70               | 15          | 70              | 30                | 82          | 88.31        | 88.63      |
| 23       | 70               | 15          | 60              | 20                | 76.62       | 86.84        | 88.67      |
| 24       | 70               | 15          | 60              | 40                | 79.61       | 90.91        | 89.66      |
| 25       | 70               | 15          | 60              | 30                | 82.19       | 91.57        | 91.47      |
| 26       | 70               | 15          | 60              | 30                | 82.19       | 91.57        | 91.47      |

The percent fixation values of Novacron Red FN-R, Novacron Yellow FN-2R and Novacron Navy FN-GN of dyed samples for optimization by using central composite design are given in Table 4.15.

#### 4.2.1 Estimated optimized recipes and estimated response values

The estimated variable levels to reach highest fixation results and estimated maximum fixation results are given in Table 4.16.  $R^2$  estimates the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error. It is also the square of the correlation between the actual and predicted (estimated) response. An  $R^2$  of 1 shows a perfect fit. In our study, high  $R^2$  values (0.85 for Fixation of Red FN-R, 0.85 for Fixation of Yellow FN-2R and 0.85 for Fixation of Navy FN-GN) showed that the estimated model fitted well with the actual data.

**Table 4.16 :** Estimated response values for optimum fixation.

| Sample ID                   | Electrolyte,<br>g/L | Alkali,<br>g/L | Temperature,<br>°C | Waiting<br>Time, min | Fixation,<br>% |
|-----------------------------|---------------------|----------------|--------------------|----------------------|----------------|
| Fixation of<br>Red FN-R     | 73.425715           | 15.766357      | 63.504479          | 31.333374            | 82.657854      |
| Fixation of<br>Yellow FN-2R | 72.421322           | 16.388368      | 61.663634          | 31.726481            | 91.905714      |
| Fixation of<br>Navy FN-GN   | 72.249419           | 16.371810      | 63.289930          | 30.451816            | 91.933989      |

The Prob > F results of the ANOVA analysis are shown in Table 4.17. The Prob > F is a good measure for significance. Prob > F is the probability of obtaining a greater F value by chance alone if the specified model fits no better than the overall response mean. Low significance probabilities are often considered evidence that there is at least one significant regression factor in the model. As shown in Table 4.17, Prob > F values are significant.

**Table 4.17 :** Prob > F values for fixation responses of optimization trials.

| Response                 | Prob > F for Trial |
|--------------------------|--------------------|
| Fixation of Red FN-R     | 0.0082             |
| Fixation of Yellow FN-2R | 0.0087             |
| Fixation of Navy FN-GN   | 0.0098             |

### 4.2.2 Actual optimized recipes and their response values

We conducted experiments by using variable levels that are approximately equal to estimated variable levels. These actual variable levels and the measured responses are also given in Table 4.18. It is apparent that measured fixation values are very close to those estimated which were given in Table 4.16.

**Table 4.18 :** Actual chemical and response values for optimum dyeing recipes.

| Sample ID                   | Electrolyte,<br>g/L | Alkali,<br>g/L | Temperature,<br>°C | Waiting<br>Time, min | Fixation,<br>% |
|-----------------------------|---------------------|----------------|--------------------|----------------------|----------------|
| Fixation of<br>Red FN-R     | 73                  | 16             | 64                 | 31                   | 82.58          |
| Fixation of<br>Yellow FN-2R | 72                  | 16             | 62                 | 32                   | 92.11          |
| Fixation of<br>Navy FN-GN   | 72                  | 16             | 63                 | 30                   | 92.00          |

The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.19.

Changing the dyeing parameters namely electrolyte concentration, alkali concentration, temperature and waiting time did not have a significant effect on color fastness results.

It could be seen that washing and water fastness results were very good. Color change and staining values for washing and water fastness tests were at least 4 on the gray scale. Staining values for perspiration fastness tests were low, on the other hand the color of the samples did not changed noticeably, except that the sample dyed at the lowest amount of electrolyte had a rating of 3/4. All dyed samples gave gray scale ratings of 5 for the dry rubbing fastness test. The wet rubbing fastness results were not good with staining on the test squares from the dyed fabrics.

It was found that all dyed samples had a rating of 2 on the blue wool fabric scale for light fastness tests.

**Table 4.19 : Color fastness results of dyeings using central composite design.**

| Sample ID | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|-----------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|           | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 1         | 5                | 4/5          | 4/5            | 4/5          | 3                            | 5            | 3                                | 5            | 5                | 4/5 | 2              |
| 2         | 5                | 4/5          | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 3         | 5                | 4/5          | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 4         | 5                | 5            | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 5         | 5                | 4/5          | 4              | 5            | 3                            | 4/5          | 3                                | 5            | 5                | 4   | 2              |
| 6         | 5                | 4/5          | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 7         | 5                | 4/5          | 4              | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 8         | 5                | 4/5          | 4/5            | 5            | 3                            | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 9         | 4/5              | 4/5          | 4/5            | 4/5          | 3                            | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 10        | 5                | 4/5          | 4              | 4/5          | 3                            | 5            | 3/4                              | 5            | 5                | 3/4 | 2              |
| 11        | 5                | 4/5          | 4              | 4/5          | 3                            | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 12        | 4/5              | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 2/3                              | 4/5          | 5                | 4   | 2              |
| 13        | 5                | 4            | 4              | 4/5          | 3                            | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 14        | 4/5              | 5            | 3/4            | 4/5          | 2/3                          | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 15        | 4/5              | 4/5          | 4/5            | 4            | 3                            | 4/5          | 3                                | 4            | 5                | 3/4 | 2              |
| 16        | 4/5              | 4/5          | 4/5            | 4            | 2/3                          | 4            | 3                                | 4            | 5                | 3/4 | 2              |
| 17        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 18        | 5                | 4            | 4/5            | 4/5          | 3                            | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 19        | 4/5              | 4            | 4/5            | 4            | 3/4                          | 3/4          | 3/4                              | 3/4          | 5                | 4   | 2              |
| 20        | 5                | 4            | 4              | 4            | 3                            | 4            | 3                                | 4            | 5                | 3/4 | 2              |
| 21        | 4/5              | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3/4                              | 4/5          | 5                | 4   | 2              |
| 22        | 4                | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 23        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3/4                              | 4/5          | 5                | 4   | 2              |
| 24        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 25        | 5                | 4/5          | 4              | 5            | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 26        | 5                | 4/5          | 4              | 5            | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |

### 4.3 Compatibility Problem in Dyeing Recipe

There would be no problem of compatibility if all dyeings could be made using single dye. But, since most shades require three different dyes, it is desirable that dyes in dyebath mixtures are as nearly completely compatible as possible. Ideally,

this means that not only do the dyes have similar solubility, give stable dyebaths, have similar fastness properties, show similar ability to migrate, but that in a particular optimal dyeing procedure, all the different dye components of the formulation will show equal percentages of exhaustion at any time during the dyeing process. If this ideal can be achieved there will be no differential strike rate, exhaustion is always on tone – i.e., the hue of the dyed goods will not vary with the time of dyeing – and there will be no differential fading or bleeding in light and washfastness tests [3].

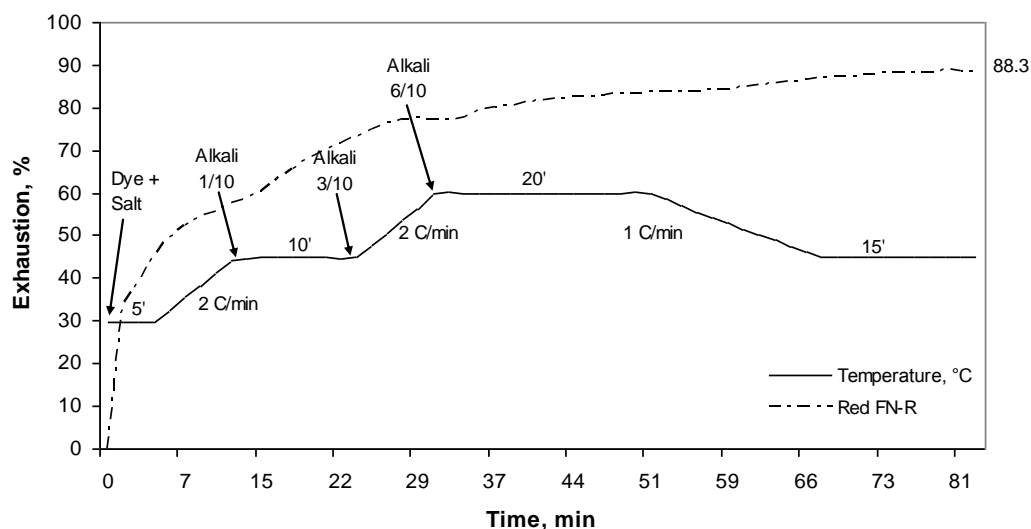
Dye manufacturers have selected preferred combinations of the dyes in attempts to meet this difficult goal. Usually they consist of three dyes, known as a trichromie, with several others for augmentation of selected properties such as color gamut.

The previous dyeings were performed using a commercial trichromatic recipe containing 0.88% o.w.f. Novacron Red FN-R, 1.26% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN with different dyeing parameters. Despite the the trichromatic recipe recommended by dye manufacturers, it is obvious that Novacron Red FN-R is not compatible with Novacron Yellow FN-2R and Novacron Navy FN-GN. In order to investigate this problem, we conducted a series dyeing with different dyeing recipes.

The following dyeings were performed at a liquor ratio of 15:1. The amounts of electrolyte and alkali used were 80 and 20 g/L respectively. After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

In the first trial, a dyeing recipe containing only 0.88% o.w.f. Novacron Red FN-R was used to observe the solo exhaustion performance of Novacron Red FN-R (see Figure 4.30).

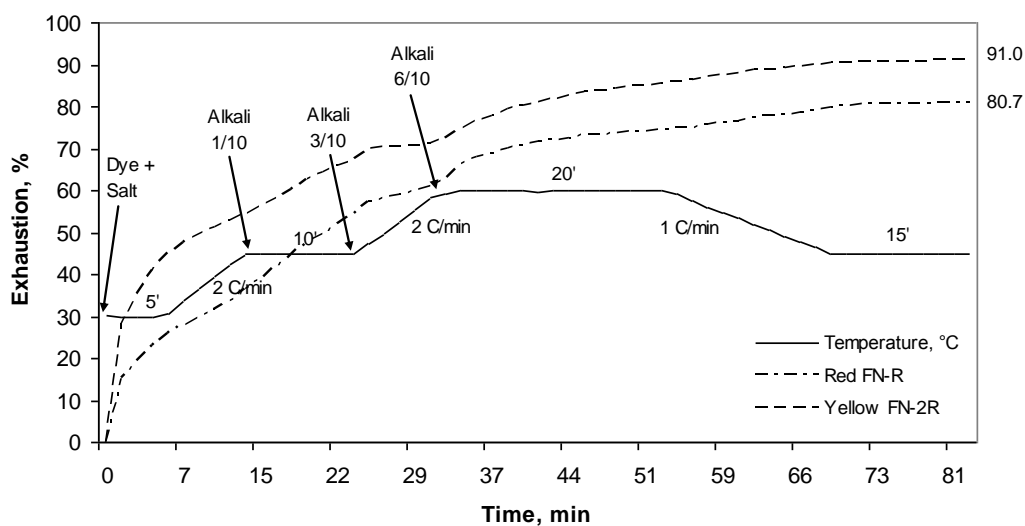
Novacron Red FN-R showed the good exhaustion performance as opposed to previous dyeings. It is apparent that Novacron Yellow FN-2R and Novacron Navy FN-GN blocked Novacron Red FN-R.



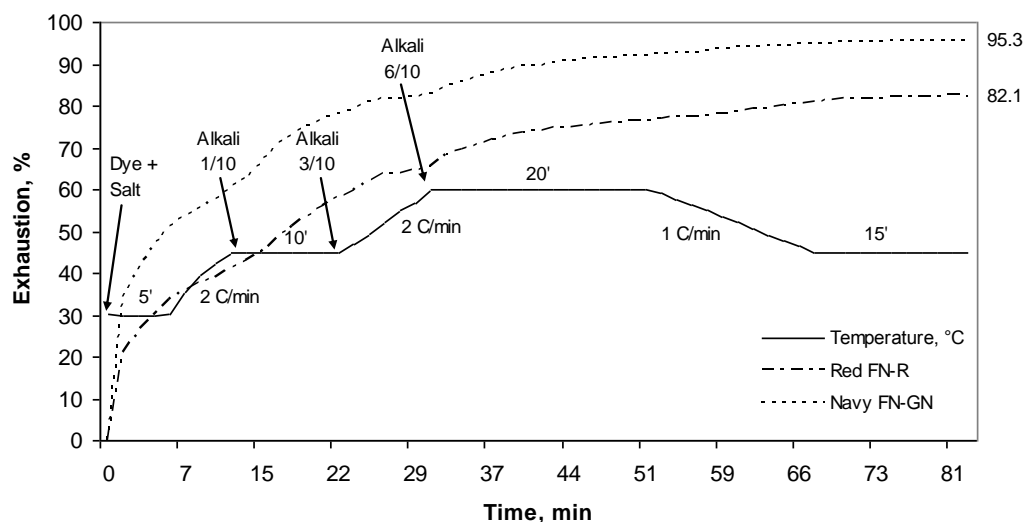
**Figure 4.30 :** The exhaustion profile of dyeing employed Novacron Red FN-R alone.

In order to investigate the dyeing performance of Novacron Red FN-R, when it was used together with Novacron Yellow FN-2R and Novacron FN-GN, two different dyeing recipes were employed.

Figures 4.31 and 4.32 show the exhaustion curves of dyeings employed two different dyeing recipes.



**Figure 4.31 :** The exhaustion profiles of dyeing employed Novacron Red FN-R and Novacron Yellow FN-2R together.



**Figure 4.32 :** The exhaustion profile of dyeing employed Novacron Red FN-R and Novacron Navy FN-GN together.

When Novacron Yellow FN-2R or Novacron Navy FN-GN were added to dyebath, the exhaustion values of Novacron Red FN-R decreased. In other words Novacron Red FN-R did not compete with other two dyes during the entire dyeing process. Therefore, a new red component (Novacron Brilliant Red FN-3GL) for trichromatic dye mixture was suggested instead of Novacron Red FN-R.

#### 4.4 Results of Central Composite Designed Experiments with New Dye

The following dyeings were performed at a liquor ratio of 25:1 using a modified trichromatic recipe containing 0.44% o.w.f. Novacron Brilliant Red FN-3GL, 0.90% o.w.f. Novacron Yellow FN-2R and 0.68% o.w.f. Novacron Navy FN-GN. Auxiliaries used in dyeings were sodium sulfate and sodium carbonate.

After dyeing, all fabrics were rinsed with hot tap water, soaped in a bath containing 2 g/L non-ionic detergent at 90°C for 20 min, then rinsed with cold tap water and finally dried at ambient temperature.

The percent fixation values of Brilliant Red FN-3GL, Novacron Yellow FN-2R and Novacron Navy FN-GN of dyed samples for optimization by using central composite design are given in Table 4.20.



**Table 4.20 :** Coded and actual design factor levels for optimization of new recipe.

| Coded ID | Electrolyte, g/L | Alkali, g/L | Temperature, °C | Waiting time, min | Fixation, %   |              |            |
|----------|------------------|-------------|-----------------|-------------------|---------------|--------------|------------|
|          |                  |             |                 |                   | B. Red FN-3GL | Yellow FN-2R | Navy FN-GN |
| 1        | 60               | 10          | 55              | 25                | 80.72         | 81.39        | 78.94      |
| 2        | 60               | 10          | 55              | 35                | 80.95         | 81.56        | 79.31      |
| 3        | 60               | 10          | 65              | 25                | 81.12         | 81.67        | 79.75      |
| 4        | 60               | 10          | 65              | 35                | 81.5          | 81.93        | 80.09      |
| 5        | 60               | 20          | 55              | 25                | 81.32         | 81.64        | 79.55      |
| 6        | 60               | 20          | 55              | 35                | 82.01         | 82.17        | 81.6       |
| 7        | 60               | 20          | 65              | 25                | 82.16         | 82.38        | 81.83      |
| 8        | 60               | 20          | 65              | 35                | 82.74         | 82.97        | 82.19      |
| 9        | 80               | 10          | 55              | 25                | 84.66         | 85.13        | 81.59      |
| 10       | 80               | 10          | 55              | 35                | 83.86         | 86.23        | 82.18      |
| 11       | 80               | 10          | 65              | 25                | 84.77         | 85.36        | 82.34      |
| 12       | 80               | 10          | 65              | 35                | 86.44         | 87.59        | 84.41      |
| 13       | 80               | 20          | 55              | 25                | 87.58         | 88.22        | 86.37      |
| 14       | 80               | 20          | 55              | 35                | 88.91         | 89.69        | 88.21      |
| 15       | 80               | 20          | 65              | 25                | 89.35         | 90.29        | 88.87      |
| 16       | 80               | 20          | 65              | 35                | 89.73         | 90.41        | 89.02      |
| 17       | 50               | 15          | 60              | 30                | 75.6          | 76.68        | 74.32      |
| 18       | 90               | 15          | 60              | 30                | 76.93         | 77.74        | 75.1       |
| 19       | 70               | 5           | 60              | 30                | 80.83         | 81.85        | 79.26      |
| 20       | 70               | 25          | 60              | 30                | 83.82         | 84.6         | 82.75      |
| 21       | 70               | 15          | 50              | 30                | 87.48         | 88.53        | 86.56      |
| 22       | 70               | 15          | 70              | 30                | 88.79         | 89.57        | 87.49      |
| 23       | 70               | 15          | 60              | 20                | 86.69         | 87.48        | 85.74      |
| 24       | 70               | 15          | 60              | 40                | 89.57         | 90.39        | 88.09      |
| 25       | 70               | 15          | 60              | 30                | 90.65         | 91.82        | 89.86      |
| 26       | 70               | 15          | 60              | 30                | 90.65         | 91.82        | 89.86      |

#### 4.4.1 Estimated optimized new recipes and estimated response values

The estimated variable levels to reach highest fixation results and estimated maximum fixation results are given in Table 4.21.  $R^2$  estimates the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error. It is also the square of the correlation between the actual and predicted (estimated) response. An  $R^2$  of 1 shows a perfect fit. In our study, high

$R^2$  values (0.92 for Fixation B. Red FN-3GL, 0.91 for Fixation Yellow and 0.92 for Fixation Navy) showed that the estimated model fitted well with the actual data.

**Table 4.21 :** Estimated response values for optimum fixation of new recipe.

| Sample ID                    | Electrolyte,<br>g/L | Alkali,<br>g/L | Temperature,<br>°C | Waiting<br>Time, min | Fixation,<br>% |
|------------------------------|---------------------|----------------|--------------------|----------------------|----------------|
| Fixation of<br>B. Red FN-3GL | 73.217606           | 16.723075      | 62.529968          | 32.403467            | 91.351734      |
| Fixation of<br>Yellow FN-2R  | 73.331097           | 16.424011      | 61.721609          | 32.098173            | 92.464800      |
| Fixation of<br>Navy FN-GN    | 72.981605           | 17.164110      | 62.205194          | 31.989878            | 90.660442      |

The Prob > F results of the ANOVA analysis are shown in Table 4.22. The Prob > F is a good measure for significance. Prob > F is the probability of obtaining a greater F value by chance alone if the specified model fits no better than the overall response mean. Low significance probabilities are often considered evidence that there is at least one significant regression factor in the model. As shown in Table 4.22, Prob > F values are significant

**Table 4.22 :** Prob > F values for fixation responses of optimization trials of new recipe.

| Response                  | Prob > F for Trial |
|---------------------------|--------------------|
| Fixation of B. Red FN-3GL | 0.0004             |
| Fixation of Yellow FN-2R  | 0.0007             |
| Fixation of Navy FN-GN    | 0.0003             |

#### 4.4.2 Actual optimized new recipes and their response values

We conducted experiments by using variable levels that are approximately equal to estimated variable levels. The results of color fastness tests namely, washing, water, perspiration (acid), perspiration (alkaline), rubbing and light are shown in Table 4.23.

Changing the dyeing parameters namely electrolyte concentration, alkali concentration, temperature and waiting time did not have a significant effect on color fastness results, even if a new dyeing recipe was used.

**Table 4.23 :** Color fastness results of dyeings using central composite design with new dyeing recipe.

| Sample ID | Washing Fastness |              | Water Fastness |              | Perspiration Fastness (Acid) |              | Perspiration Fastness (Alkaline) |              | Rubbing Fastness |     | Light Fastness |
|-----------|------------------|--------------|----------------|--------------|------------------------------|--------------|----------------------------------|--------------|------------------|-----|----------------|
|           | Staining         | Color Change | Staining       | Color Change | Staining                     | Color Change | Staining                         | Color Change | Dry              | Wet |                |
| 1         | 4/5              | 4/5          | 4/5            | 4/5          | 3                            | 5            | 3                                | 5            | 5                | 4/5 | 2              |
| 2         | 4/5              | 4/5          | 4/5            | 4            | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 3         | 4/5              | 4/5          | 4              | 4            | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 4         | 4/5              | 4/5          | 4              | 4            | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 5         | 4/5              | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 5            | 5                | 4   | 2              |
| 6         | 4/5              | 5            | 4              | 5            | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 7         | 4/5              | 4/5          | 4/5            | 4            | 3                            | 4/5          | 3                                | 4/5          | 5                | 4   | 2              |
| 8         | 4                | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 9         | 4/5              | 4/5          | 4/5            | 4            | 3                            | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 10        | 4/5              | 4/5          | 4/5            | 5            | 3                            | 5            | 3/4                              | 5            | 5                | 3/4 | 2              |
| 11        | 4/5              | 4            | 4/5            | 4            | 3                            | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 12        | 4                | 4            | 4/5            | 4            | 3                            | 4/5          | 2/3                              | 4/5          | 5                | 4   | 2              |
| 13        | 4/5              | 4/5          | 4/5            | 4            | 3                            | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 14        | 4                | 4/5          | 4/5            | 4            | 2/3                          | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 15        | 4/5              | 4            | 4/5            | 4            | 3                            | 4/5          | 3                                | 4            | 5                | 3/4 | 2              |
| 16        | 4/5              | 4/5          | 4/5            | 4            | 2/3                          | 4            | 3                                | 4            | 5                | 3/4 | 2              |
| 17        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4            | 3/4                              | 4/5          | 5                | 3/4 | 2              |
| 18        | 5                | 4            | 4/5            | 4/5          | 3                            | 4            | 3                                | 4/5          | 5                | 3/4 | 2              |
| 19        | 4/5              | 4            | 4/5            | 4            | 3/4                          | 3/4          | 3/4                              | 3/4          | 5                | 4   | 2              |
| 20        | 5                | 4            | 4              | 4            | 3                            | 4            | 3                                | 4            | 5                | 3/4 | 2              |
| 21        | 4/5              | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3/4                              | 4/5          | 5                | 4   | 2              |
| 22        | 4                | 4/5          | 4/5            | 4/5          | 3                            | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 23        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3/4                              | 4/5          | 5                | 4   | 2              |
| 24        | 5                | 4/5          | 4/5            | 4/5          | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 25        | 5                | 4/5          | 4              | 5            | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |
| 26        | 5                | 4/5          | 4              | 5            | 3/4                          | 4/5          | 3                                | 4/5          | 5                | 3/4 | 2              |

These actual variable levels and the measured responses are also given in Table 4.24. It is apparent that measured fixation values are very close to those estimated which were given in Table 4.21.

**Table 4.24 :** Actual chemical and response values for optimum dyeing recipes with new red dye.

| Sample ID                    | Electrolyte,<br>g/L | Alkali,<br>g/L | Temperature,<br>°C | Waiting<br>Time, min | Fixation,<br>% |
|------------------------------|---------------------|----------------|--------------------|----------------------|----------------|
| Fixation of<br>B. Red FN-3GL | 73                  | 17             | 63                 | 32                   | 91.17          |
| Fixation of<br>Yellow FN-2R  | 73                  | 16             | 62                 | 32                   | 92.26          |
| Fixation of<br>Navy FN-GN    | 73                  | 17             | 62                 | 32                   | 90.42          |

## 5. CONCLUSION

The increased public awareness and concerns about the environmental impact of the coloration industry, the increased cost of energy, labor, water and auxiliaries as well as the associated costs of processing colored effluents necessitate the optimization and control of all factors influencing the uptake of dye by fiber, including temperature, auxiliaries, time, liquor to goods ratio. All these factors in the dyeing process are the most well established influential factors affecting the depth of shade of dyed goods as well as the uniformity of the coloration process. Despite myriad work conducted over the last several decades to elucidate the role of individual dyeing parameters on the outcome of dyeing, it has only recently become possible to investigate the exhaustion profile of individual dyes in an admixture in real time as a function of various parameters.

Cotton fabric was dyed with a commercially recommended trichromatic set of fiber reactive dyes at three different fixation temperatures. Also two alkali addition methods were applied. A real time dyebath monitoring system was employed to obtain individual dye's exhaustion profiles during the dyeing process. Data acquisition software was used to calculate the total exhaustion of dye and subsequently dye fixation for each dye was also calculated. Portionwise addition of alkali gave better results in comparison with addition of alkali in one portion. When the fixation temperature was increased, the dye uptake values of Novacron Red FN-R and Novacron Yellow FN-2R decreased, but the dye uptake values of Novacron Navy FN-GN increased. Apart from the addition of alkali, the optimum dyeing temperature was found as 60°C. Portionwise addition of alkali at fixation temperature gave the highest exhaustion results. The changing the alkali addition method is less effective for Novacron Yellow FN-2R.

In order to investigate the effect of temperature gradient and cooling step, a series dyeing was conducted with two different temperature gradients and with or without the presence of cooling step. It was found that temperature gradient had no effect on

dyeing performance whereas adding cooling step improved the exhaustion levels for all three dyes.

A new temperature-time profile, in other words dyeing procedure was offered. In new procedure, first two portions of alkali were added during the heating up. The new procedure gave better results in compare with the previous procedure.

In order to set the base levels of factors in the central composite design, a set of dyeing were done using different electrolyte and alkali levels. It was found that the highest fixation values were achieved when the concentrations of electrolyte and alkali were 70 and 15 g/L.

In order to examine the effect of variations in liquor to goods ratio on performance of a set of a commercially recommended trichromatic recipe of fiber reactive dyes, cotton fabrics were dyed at different liquor to goods ratios. All dyeing parameters, with the exception of liquor to goods ratio were kept identical. The liquor to goods ratio was varied from 50:1 to 30:1, 25:1, 20:1 and finally 15:1. The application of real time dyebath monitoring device demonstrated that Novacron Red FN-R is not compatible with the other two dyes used in this trichromatic dye set. Indeed when the liquor to goods ratio was decreased from 50:1 to 15:1 the difference in the final exhaustion level of Novacron Red FN-R and that of Novacron Yellow FN-2R and Novacron Navy FN-GN dyes dropped from approximately 21% at a liquor to goods ratio of 50:1 to approximately 13% at a liquor to goods ration of 15:1. In terms of dye fixation, results showed that all three dyes exhibited maximum fixation at a liquor to goods ratio of 25:1 and that a further reduction in liquor to goods ratio adversely influenced the total amount of dye fixed.

A central composite design was used to optimize the dyeing parameters including electrolyte concentration, alkali concentration, temperature and waiting time.

A new trichromatic recipe was offered to overcome the compatibility problem. Novacron Brilliant Red FN-3GL was used instead of Novacron Red FN-R as red component of trichromatic recipe. Novacron Brilliant Red FN-3GL was a very good substitute, because the exhaustion and fixation levels compete with the Novacron Yellow FN-2R and Novacron Navy FN-GN.

## **6. FUTURE WORK**

Increasing global competition and environmental awareness has prompted the dyeing industry to offer environmentally benign solutions that are combined with enhanced production efficiency. Cotton remains the most important natural fiber worldwide and thus improvements in the dyeing of cotton can result in significant environmental gains. Reactive dyes are widely used for the coloration of cotton substrate but many exhibit relatively poor exhaustion and fixation properties.

In this study, we started with screening the effects of dyeing parameters, including electrolyte, alkali, temperature and time on dyeing behaviour in terms of exhaustion and fixation as well as on color fastness values.

We conducted experiments according to a central composite design and offered and optimum recipe to reach as high fixation values for each dye in trichromatic dyeing recipe as possible.

Our results offered enlightening information about compatibility of each dye in trichromatic dyeing recipe. The results of this study may be used as a starting point for detailed further studies on in-depth determination of the mechanism of incompatibility.

In addition, the study demonstrated the effectiveness of real time monitoring and data acquisition systems as a means of generating suitable control strategies for various dye-fiber combinations.





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### List of Publications and Patents:

- **Ozturk, M.** & Nergis, B.U., “Determining the Dependence of Colour Values on Yarn Structure”, Coloration Technology, Vol 124, No 3, 145-150, 2008
- **Ozturk, M.**, Shamey, R. & Dayioglu, H., “Role of Alkali and Fixation Temperature on Dye Uptake in Reactive Dyeing of Cotton”, 2011 AATCC International Conference, Charleston, SC, USA, 22-24<sup>th</sup> March 2011
- Gunay, M. & **Ozturk, M.**, “Measurement and Characterization of Dyeing Levelness”, Textile Futures Conference 2008, Raleigh, NC, USA, 13-15<sup>th</sup> August 2008
- **Ozturk, M.**, “Reactive Dyeing Properties of Bamboo Fiber”, 3<sup>rd</sup> International Textile, Clothing & Design Conference, Dubrovnik, Croatia, 8-11<sup>th</sup> October 2006
- **Ozturk, M.**, “Dyeing Characteristics of Bamboo Fiber With Reactive Dyes”, 6<sup>th</sup> Autex (Association of Universities for Textiles) World Conference 2006, NCSU, Raleigh, NC, USA, 11-14<sup>th</sup> June 2006
- Kalav, B. & **Ozturk, M.**, “Antibacterial Finishing Processes of Textile – Literature Survey”, 1<sup>st</sup> Istanbul International Textile and Textile Machinery Congress, Istanbul, Turkey, 1-2<sup>nd</sup> June 2006
- **Ozturk, M.** & Dayioglu, H., “The Effect of Electrolyte Concentration on Colorfastness Properties of Dyed Cotton Fabrics”, International Symposium Present and Perspective in Textile Engineering, Iasi, Romania, 10-12<sup>th</sup> November 2005

- **Ozturk, M.** & Dayioglu, H., “The Influence of Electrolyte Concentration on Dyeing Cotton Using Reactive Dyes”, 5<sup>th</sup> International Istanbul Textile Conference, Istanbul, Turkey, 19-21<sup>st</sup> May 2005
- **Ozturk, M.** & Dayioglu, H., “Effect of Functional Groups of Reactive Dyes on Color Fastness Properties of Dyed Cotton Fabrics”, 2<sup>nd</sup> International Textile, Clothing & Design Conference, Dubrovnik, Croatia, 3-6<sup>th</sup> October 2004

#### **PUBLICATIONS/PRESENTATIONS ON THE THESIS**

- **Ozturk, M.**, Dayioglu, H. & Shamey, R., “Effect of Liquor to Goods Ratio Variation on Sorption of Reactive Dye Recipe Components on Cellulose”, AATCC Review, Vol 12, No 1, pp. 48-53, 2012