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Review Paper

Eco-Friendly Dyeing Process of Cotton Fiber with Reactive Dyes

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ABSTRACT

The aim of this study research is to present the idea of the level of the research the research being done in the area of eco-friendly dyeing of cotton. This research discusses cotton and its polymer structure at first and then the properties of cotton fiber. This paper also briefly describes the terminology of dyeing. It is followed by the consequences of dyeing and its hazards on the environment. The technological development for the reactive dye structure, dyeing machines, dyeing process, chemical modification and alternative dyeing auxiliaries have also been discussed. Prog. Color Colorants Coat. 9 (2016), 61-70 © Institute for Color Science and Technology.

1. Introduction

Cotton is being used as a textile fiber since 7000 years. Cotton fiber belongs to gossypium family [1]. Although, numerous synthetic fibers such as polyesters, acrylics, polyamides and polypropylenes have entered the market over the past 50 years, cotton has still maintained its strong consumer demand worldwide [2]. Today, the textile goods made up of cotton covers nearly half of the total textile market, and the demand is expected to be increased further cotton textiles represent more than half of the global textile market, and the demand is expected to continue [3]. This dominance of cotton fiber is mainly due to its natural comfort, performance, appearance and versatility and another factor is product and fabric development. Cotton fiber was being cultivated in Indus Valley civilization [4]. People at Moen-jo-Daro were used to cultivate cotton fibers on river bank of Indus. Cotton fiber has gained its position due to flexibility, fitness, fineness and spinnability. The cotton has remained dominating textile fiber due to its natural comfort, performance and appearance. The cultivation of cotton is being focused, and the yield of cotton crop is going to be increased. The cotton fiber is among those textile fibers which finds its application in all areas of textiles. Natural comfort, performance and appearance of cotton fiber dominate the cotton over many other textile fibers. Crop production of cotton fiber is increasing day by day. It is expected that cotton production will increase more and more in few years. Cotton is used in all stages of textiles i.e. fiber, yarn, fabric and garments.

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2. Structure and Properties of Cotton

The fiber is a single plant cell found as the seed hair of a genus of the plants called gossypium [5]. Cotton fiber consists of cuticle, primary cell walls, secondary cell walls and lumen, as shown in Figure 1.The cuticle is the very outside or 'skin' of the fiber, and it is composed of pectin, protein and waxes [6]. So, it makes the fiber hydrophobic unless a wetting agent is used. The primary cell wall is immediately underneath the cuticle. The secondary wall, beneath the primary wall, forms the bulk of the fiber.

Cotton fibers may be classified into three categories i.e. mature fibers, immature fibers and dead fibers. The difference among these three is for their secondary cell wall, this secondary cell wall is well developed in mature fiber, inadequate in immature fibers and absent in dead fiber, The development of secondary cell walls is inadequate in immature fibers whereas dead a fiber does not contain it. During mechanical processing, immature and dead fibers entangle with one another and form the neps. The dye uptake of immature fibers is poor than mature fibers, thus the immature fibers are dyed paler than mature fibers; also it has been observed that the dead fibers remained nearly undyed after the dyeing process. Dye is not penetrated in immature fibers as good as in mature fibers, and they cannot appear as dark as mature fiber and dead fibers remains undyed [8]. The immature and dead fibers tend to become entangled into small fibrous bundles, called neps, during the mechanical processes for producing yarns [9]. Neps are appeared as white and light spots after dyeing. Mercerization is carried out to swell immature fiber to avoid white and light spots. Primary and secondary walls are composed of fibrils. The fibrils occur in the spiral form at certain angles to the fiber axis [10]. The lumen is a longitudinally hollow canal in the center of the fiber. Cotton fiber has unique physical structure. It has convolution on its surface which provides cohesiveness and helps in spinning process. Cross-sectional view of cotton fiber is kidney shaped [11], which makes cotton fiber comfortable and more absorbent, as shown in Figure 2.

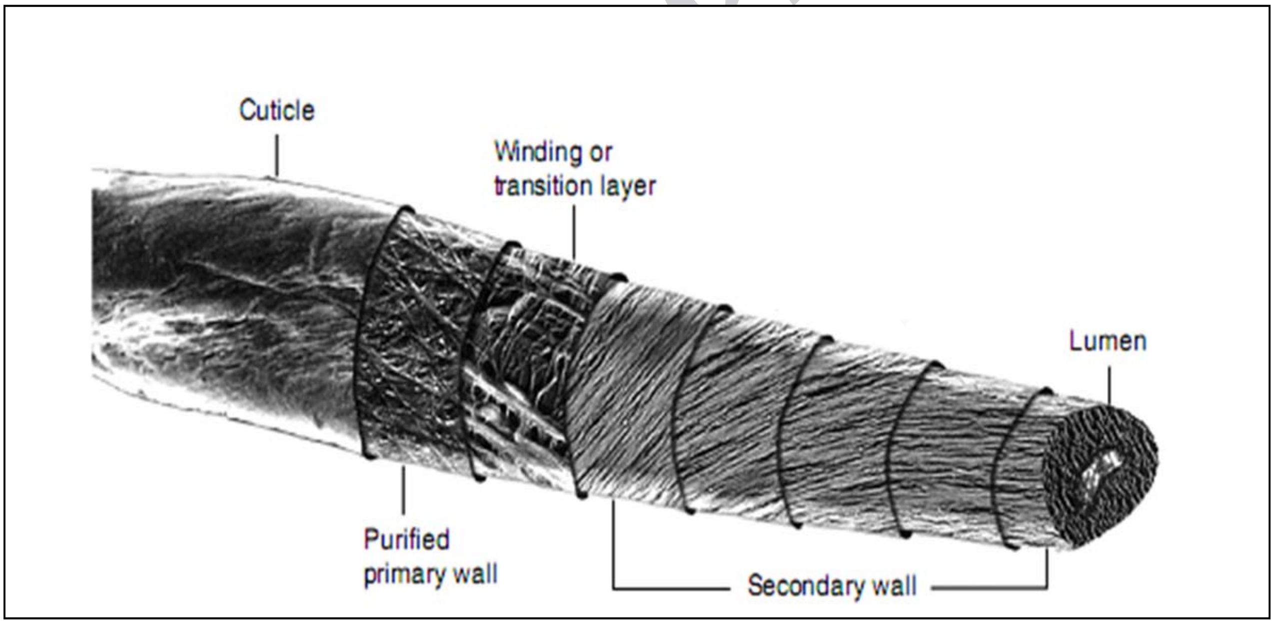

Figure 1: A morphological diagram of the cotton fiber [7].

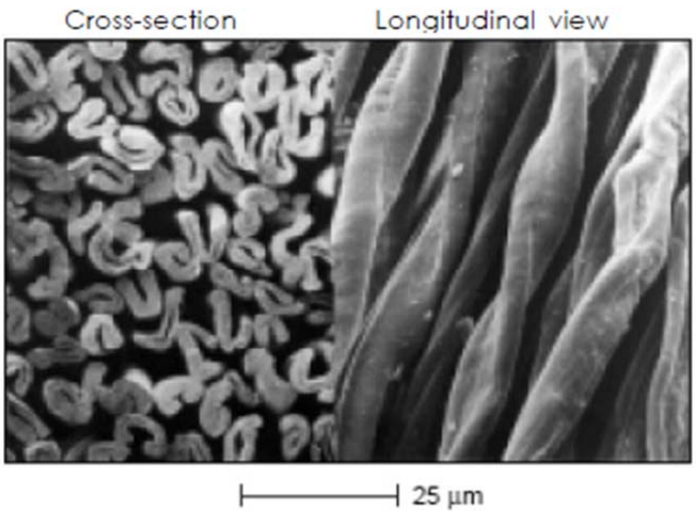

Figure 2: Scanning electron micrographs of raw cotton fibers [12].

3. Cotton Polymer and Fiber Polymer System

Cotton fibers are composed of cellulose polymers, mostly α-cellulose [13] and its repeating unit is cellobiose [14], as shown in Figure 3. Cotton fiber has degree of polymerization about 5000 according to its cellobiose unit. Cotton polymer system is highly crystalline and oriented [15]. Hydroxyl and methylol are important functional groups of cotton cellulose. The presence of abundant hydroxyl groups and the polymer chain conformation causes inter- and intra-molecular hydrogen bonds which enhances stiffness of fibers whereas Vander walls forces are of little significance.

4. Properties of Cotton Fiber

4.1. Hygroscopic Properties

Cotton fiber is hydrophile and water absorbent because polar hydroxyl groups attracts polar water molecule. Cotton fiber structure allows the penetration of water between the fibrils of cotton fiber where they may form hydrogen bonds [16]. Because of the amorphous region of cotton fibers, cotton easily dyed even the size of dye molecule is moderately large.

The moisture regain of cotton is 8.5%[17]. At room temperature where relative humidity is 100% the moisture regain increases up to 25-30%. On absorbing moisture, secondary wall of cotton fiber swells and get strength mostly due to temporary improvement in its amorphous region. When Cotton fiber absorbs moisture, it becomes swells because of the swelling of secondary wall. Some of these fibers give strength when wet. This is because of the temporary improvement in the amorphous region.

4.2. Chemical Properties

In cotton cellulose, chemical reactions occur due to the hydroxyl groups. Most of the chemical reactions occur inon the crystalline region. Reactions are classified into two categories

1. Esterification
2. Etherification

4.2.1. Esterification

This process takes place under acidic conditions which mainly include nitration, acetylation, phosphorylation, and sulfation..

4.2.2. Etherification

This process takes place under alkaline conditions. This reaction is only source of reactive dyeing. In alkaline conditions, cellulose behaves as a weak acid and the formation of cellulosate anion is eased. Covalent bond formation between dye and fiber is achieved by nucleophilic addition or nucleophilic substitution reactions. Etherification should not be confused with mercerization process. Mercerization is a fifth step of pretreatment process carried out to enhance luster , tensile strength and dye uptake of cotton fiber under strong alkaline conditions.

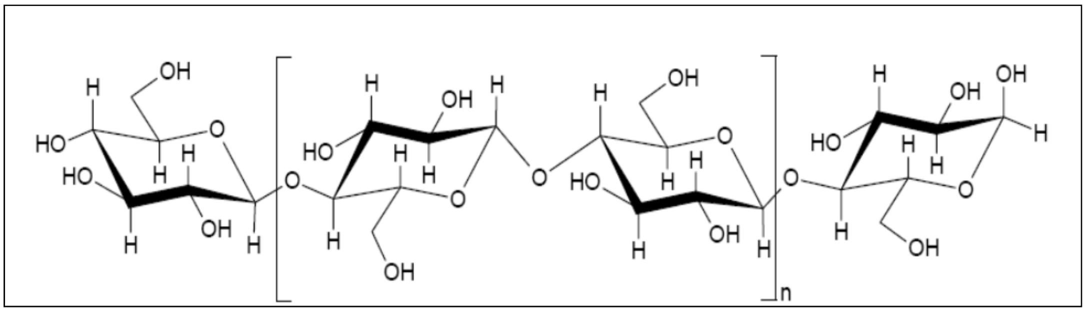

Figure 3: Molecular structure of cellulose.

4.3. Thermal Properties

Cotton fiber conducts heat but higher temperature (i.e. 150 °C) may lead to browning and hardening of the fibers [18]. Excessive heating may cause decomposition and dehydration of cellulose.

4.4. Tensile Properties

The good cohesiveness of cotton fiber, larger number of hydrogen boding between two polymers with in the fiber and between two fibers with in a specimen, higher molecular weight and higher crystalline to amorphous ratio are some important causes for good tensile properties of cotton fiber. The cotton fiber is preferred over other fibers due to it better tensile properties. Tensile strength and cohesiveness of cotton fiber enhances it's overall mechanical properties.

5. Dyeing of Cotton

Cotton fiber is dyed with direct, vat, sulfur, azo and reactive dyes. When cotton cellulose is immersed in water, negative zeta potential charge is appeared on the surface of the fiber [19]. Dyeing with Vat and sulfur dyes is accomplished by physical retention of dye molecules within the fiber. These dyes are initially reduced to smaller size and then hydrolyzed back to their original molecular size in the amorphous region of cotton cellulose. Cotton fiber may be dyed by azo dyes which follow the following steps, naptholation, diazotization, coupling or developing. Moreover, cotton is dyed with direct and reactive dyes mostly. These are anionic dyes and thus they are exhausted to the fiber by aid of salt.

5.1. Reactive Groups according to their reactivity

The reactive groups can be categorized according to their reactivity. Some of the reactive groups are shown in Figure 4. The comparative study of these reactive groups can be understood using Table 1.

5.2. Dye substantivity

The term 'substantivity' was originally derived from popular substantive dyes (Direct dyes). The substantivity may be defined as the ability of dye molecule to move from liquid medium to textile specimen. The quantitative measurement of the force with which the dye is captured by the fiber is determined as 'affinity'. However, substantivity is often used as a qualitative description of the affinity of a dye for a particular fiber.

The substantivity of a dye generally depends on its solubility, molecular size and structure. Substantivity is favored by the formation of multiple dye-fiber bonds. In reactive dyeing of cotton, these bonds are hydrogen and covalent bonds. Thus, reactive groups also exert significant effect on the substantivity.

5.3. Dye exhaustion

In exhaust dyeing, the fiber starts absorbing the dye as soon as it is immersed into the dye liquor. As a result, the concentration of dye in the dye bath decreases gradually. This shift of dyes towards the fiber is generally referred to as exhaustion. The degree of dye bath exhaustion as a function of time describes the rate and extent of dyeing process, as mentioned in equation 1. For a single dye, the exhaustion is expressed as the mass of dye taken up by the fiber divided by the total mass of the dye originally used in the dye bath of constant volume.

$$\%Exhaustion = [(C_o - C_s) / C_o] \times 100 \qquad (1)$$

Where, Co and Cs are the concentrations of dye in the dye bath initially and at some time later during the process, respectively.

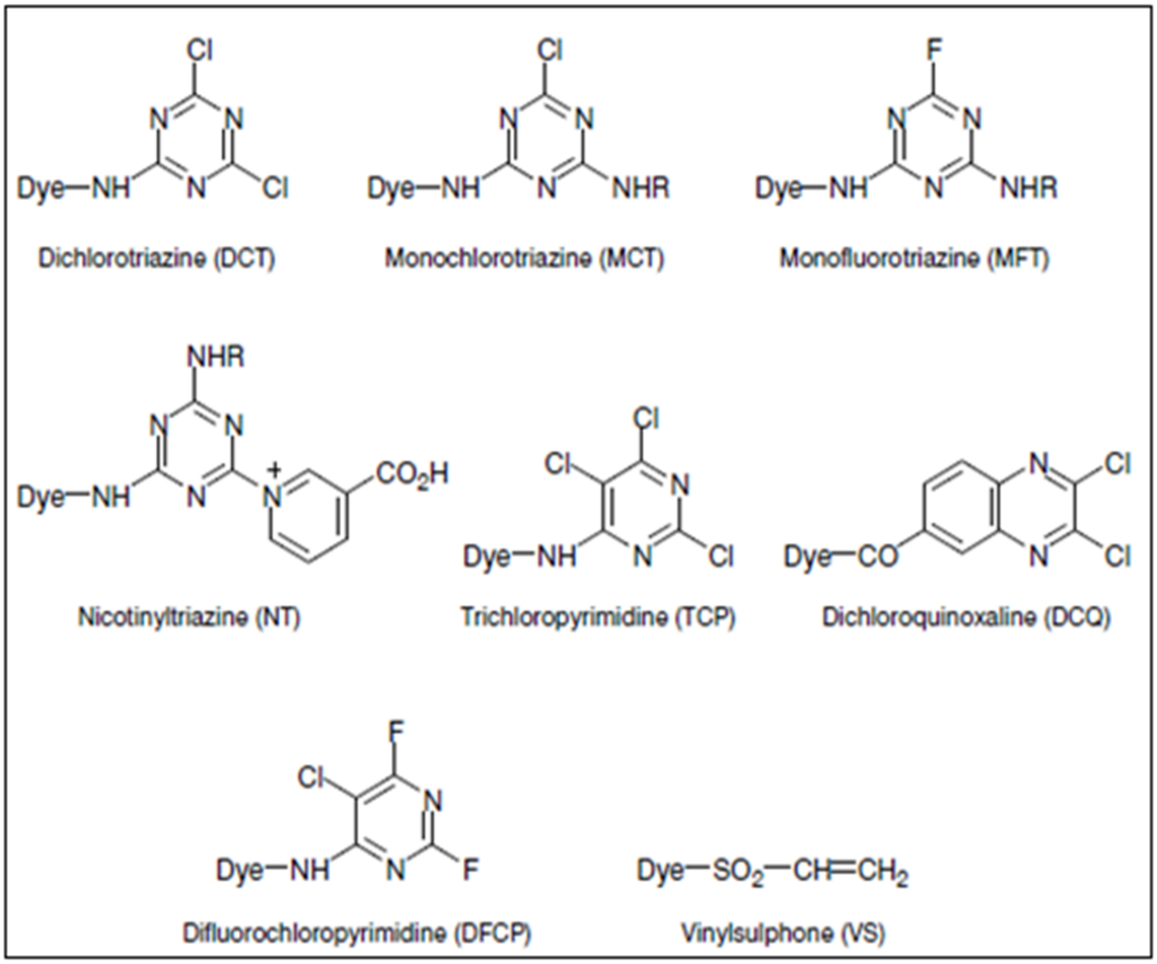

Figure 4: Different types of Reactive groups [20].

Table 1: Comparative study of reactive groups according to their reactivity.

High reactive groups	Medium reactive groups	Low reactive groups
used for exhaust application	used for continuous application [19]	Used for continuous application
TFP (Tri floro pyrimidine) and DFCP based	DCT (Di chlorotriazine) and MCT (mono chlorotriazine) based	VS (vinyl sulfone) based
Relatively expensive and are not used for localized application mostly	Have medium price, so could be considered as reasonable price	have lowest price and are used for localized application

5.3. Dye diffusion

The penetration of a dye into the fiber polymer system from the dye-fiber interface is known as dye diffusion. Fick's second law states that the rate at which the dye diffuses across a unit area in the fiber is proportional to the concentration gradient across that area, the proportionality constant being the diffusion coefficient [21]. The coefficient of diffusion is a parameter used in most fundamental studies on dye diffusion. The extent of dye diffusion as a percentage of the total dye on the fiber has not been generally reported.

5.4. Dye fixation

There are three main ways in which dye molecules can become attached (fixed) to the cotton fiber: mechanical retention, physical bonding and chemical reaction. Vat, sulfur and azoic dyes are fixed principally with mechanical retention, i.e. the dye molecules are trapped in an insoluble pigmentary form within the fiber polymer system. Direct dyes are fixed with physical hydrogen bonding and Vander Waal's forces. Reactive dyes are fixed mainly by reaction with the fiber polymer leading to the formation of covalent bonds.

Dye fixation is generally determined as an estimate of the average proportion of dye actually fixed on a textile fiber. The lower fixation levels of reactive dyes are essentially due to unavoidable dye hydrolysis during dyeing. There have been various analytical ways for estimating the extent of dye fixation and dye hydrolysis. Today, the percentage of dye fixation is usually determined by using absorbance measurements of dye bath solution and/or color strength measurements of the fabric during dyeing.

5.5. Exhaust Dyeing

Exhaust dyeing is a process of immersion of the fabric in the dye bath, transfer of the dye to, and its gradual diffusion into, the fiber, so that the dye bath concentration decreases. A general exhaust dyeing process with washing off process of cotton fabric dyed by fabric reactive dyes is shown in Figure 5. In the typical exhaust dyeing of cotton with reactive dyes, the first phase of dyeing is carried out under neutral pH conditions to allow dye exhaustion and diffusion. This promotes uniform coloration. Fixation of the dye is then achieved by adding a suitable alkali to the dye bath, either completely or gradually, to activate the cellulosate anions. The reaction phase of the dyeing occurs over 30–60 min with typical dyeing temperatures within the range from 30 °C to 90 °C, depending upon the type of reactive group and its reactivity.

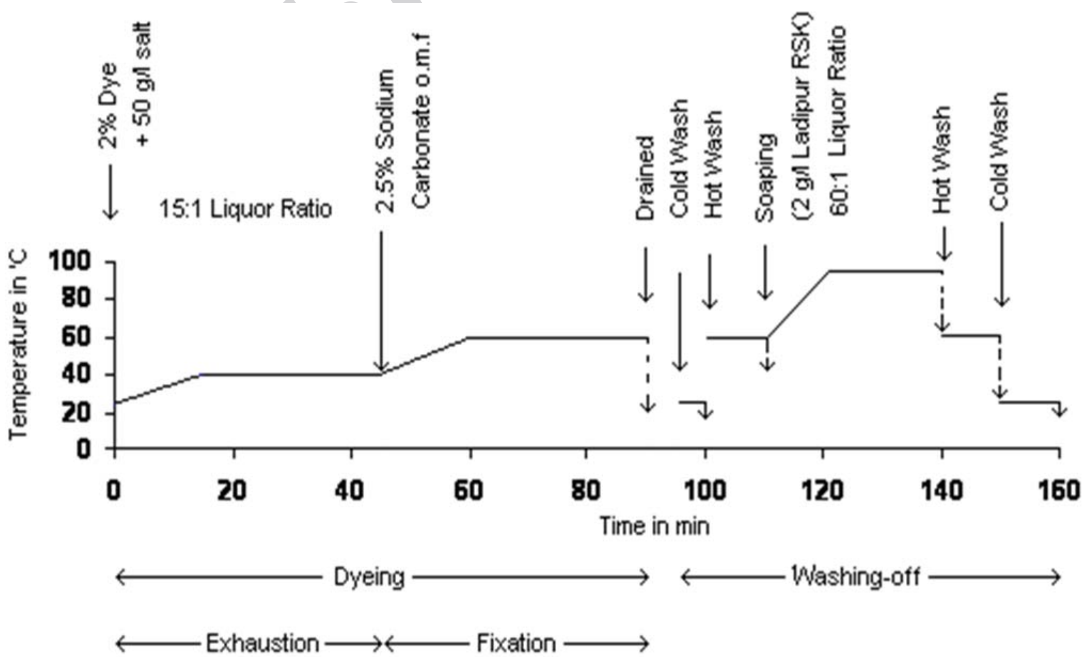

Figure 5: General Exhaust Dyeing with washing off process of cotton fabric dyed by fabric reactive dyes.

The fixation process results in additional dye transfer to the fiber which is often referred to as secondary exhaustion. The secondary dye exhaustion and dye-fiber reaction then progress until no additional dye is taken by the fiber. The important parameters in exhaustive reactive dyeing are the liquor-to-fiber ratio, temperature, pH and time.

5.4. Continuous Dyeing

The continuous dyeing is also one the important methods for dyeing of cotton fibers. The continuous dyeing is done by the aid of padder. There are different methods used in continuous dyeing used for the dyeing of cotton fabrics i.e. Pad dry cure, pad dry steam, etc. A Continuous dyeing process typically consists of the following; Dye application, dye fixation with heat or chemicals and finally washing. Continuous dyeing has been found to be most suitable for woven fabrics.

5.5. Washing off

After completion of the dye exhaustion and dye-fiber reaction phases, the fabric contains covalently-bonded dye, unreacted absorbed dye, and hydrolyzed dye. The unreacted and hydrolyzed dyes are generally referred to as unfixed dyes, and the process of removing these unfixed dyes is known as washing off [22]. The fabric also contains residual electrolyte and alkali which should be removed. The unfixed dye is weakly trapped within the fiber through hydrogen bonds and Vander Waal's forces which can be desorbed easily during washing by the consumer of the dyed cotton textiles. In other words, the presence of unfixed dye in a reactive dyed fabric gives poor washing fastness. Thorough washing-off after dyeing of reactive dyed cotton is therefore essential to remove all of the unfixed dye, residual electrolyte and alkali. This washing-off is a series of thorough rinsing including boiling with a detergent. This needs large amounts of high quality water. In traditional reactive dyeing, about three quarters of the total water is consumed for washing-off step.

6. Reactive Dyeing Effluent

There is high demand to keep this globe green, which is pronounced not only by environmentalists but by every person living and loving this globe [23]. Generally, the wastes can be classified into two ways: the physical form, i.e. gas, liquid or Solid and their effect on the environment, i.e. toxicity and biodegradability. Toxicity is the degree to which any substance is poisonous for life in any way. Biodegradability is discussed in the next section. The dyeing of cotton generates toxic aqueous waste, that is needed to be treated before discharging into environment [24]. The textile processing effluent wastes are mostly in liquid form and can be further classified according to Figure 6.

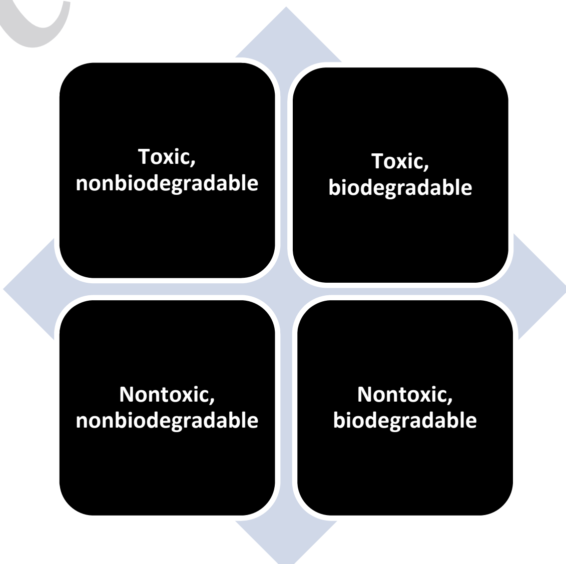

Figure 6: The toxicity versus biodegradability matrix of the reactive dye effluent.

The reactive dyeing effluent is essentially composed of the left over dye bath solution, and the draining washing-off water containing the residual dye, inorganic electrolyte and inorganic alkali taken from the dyed fabric, and also the detergent. This effluent is mostly drained to the rivers and seas after a small treatment and sometimes without treatment. This effluent increases the salinity of the effluent to very high levels which adversely affects the life forms in water, and the life that consumes that water.

The term Biodegradability means “The ability of any substance to be biodegradable”. The substances which are biodegradable are broken down into simpler molecules [25], by the digestive action of micro-organisms that are capable of using them as food. These simpler molecules are then excreted as waste, which may form a food source for some other organism, to be then converted into yet simpler molecules which are excreted, and so forth. All of the dissolved components in reactive dyeing effluent are more or less toxic to the environment. However, the major environmental concern is the inorganic electrolyte (sodium chloride or sodium sulfate) because it is classified as potentially toxic and nonbiodegradable.

Suitable alternative compounds, which are both nontoxic and biodegradable, or of low toxicity but biodegradable to nontoxic substance(s), can be used to reduce this problem. This current research forms a part of such efforts where inorganic electrolytes and alkalis are replaced by alternative biodegradable organic compounds. Total dissolved solids (TDS) are a measure of the total amount of dissolved substances per unit volume of water. This is directly proportional to any characteristic parameter of the substances such as salinity and conductivity in the case of dissolved inorganic electrolytes. Thus, reduction of the total dissolved solids (TDS) content of an effluent would lead to reductions in other environmental concerns such as salinity, conductivity and oxygen demands.

7. Development of Reactive Dyeing Of 7. Cotton Textiles to Reduce Effluent Pollution

7.1. Development of reactive dyes

Two approaches were proposed to achieve the bond formation between dye and fiber i.e. synthesizing dye within the fiber cellulose and making a dye which may react with cellulose fiber. Azo dyes followed the first strategy and reactive dye obeyed the second one. Procion dyes by ICI were first commercialized in 1950s. Alkali conditions were required for this dyeing strategy. Alkali condition dissociates the OH of cellulose fiber and forms cellulosate anion capable of reacting with dye molecule. A large variety of reactive groups have been synthesized so far to reduce dyeing temperature, dyeing time, and effluent load.

7.2. Development of dyeing machine and process

The early liquor ratio to achieve dyeing was up to 1:20. But soon it was realized that effluent control may be achieved by reducing liquor ratio. Various approaches were made for minimizing liquor ratio i.e. development of soft flow which minimized the liquor ratio to 1:5 for exhaust process. Continuous dyeing process minimizes the liquor by half of the weight of fabric i.e. 1:0.5. Cationization of cotton also played another strategy for minimizing effluent load [26]. Cationization of cotton had also its drawback as cationization is not fully eco-friendly process. Dye itself has been modified and various reactive groups are synthesized. Not only various groups but also bifunctional and polyfuctional reactive dyes are synthesized. Increasing functional groups enhances the probability for dye to be attached on the fiber. Another important strategy which is followed in this study is the use of biodegradable salts. These salts are non-toxic and being biodegradable, so they lessen the salinity of water.

7.3. Chemical modification prior to dyeing

The increasing awareness of environmental protection drives dyes manufacturer to explore new eco-friendly textile processing techniques. In Reactive dyeing process of cellulosic fiber, substantial quantities of electrolytes such as sodium chloride and sodium sulfate are required to increase the dye-uptake of reactive dye, but the inorganic salts in dyeing waste water are difficult to be biodegraded. Exhaust dyeing with 10:1 liquor to material ratio needs a salt concentration of 30-80 g/l. This corresponds to 300-800 g salt per kg of dyed cotton. During effluent treatment, only a small quantity of salt is removed thus the major quantity of salt enters in to the environment. High salt concentration in effluent has the following disadvantages:

1. Rivers and lakes get polluted.
2. Fresh water organisms can have toxic effects.
3. In the regions with scarce fresh water resources, such water has to be used for irrigation and agriculture.
4. If salts concentration is too high, soil may become overloaded with salt, making the land infertile and ultimately useless.

The dyes manufacturers have made great efforts to decrease the amount of inorganic salts used in dyeing process of textile. They have worked on modification of reactive dyes which need very low amount of salt for exhaustion; these dyes are often called as low-reactive dyes. Dyes manufacturers then introduced modified reactive dyes such as Cibacron LS dyes which require only 20 g/l salt, where as the conventional reactive dyes require 60-80 g/l salt for exhaustion. In recent years, many dyeing workers tried some biodegradable and non poisonous dyeing additives to substitute inorganic salts such as Ethylenediamine tetra-acetic acid (sodiumedate) and Trisodiumnitrilotriacetate (Trisodium NTA) as exhausting agent in dyeing of cotton with reactive dye.

7.4. Use of biodegradable organic compounds in dye bath formulation

Reactive dyes are the most popular dye class for dyeing of cellulosic fabric especially for cotton fabric. These dyes offer several advantages such as low cost, ease of application, wide gamut of color and good fastness to light, washing and rubbing. However, in case of reactive dyes, high concentration of salt are required for effective exhaustion of dye onto the cotton surface.

Different approaches have been adopted to reduce salt during dyeing such as modification of dye structure, cationization of cellulose through deposition or chemical reaction with polymeric compounds containing cationic groups.

One of the most interesting strategy being practiced nowadays is to replace the inorganic salts and other compounds with eco-friendly biodegradable organic compounds. These organic biodreable compounds used during dyeing may be degraded biologically with the passage of time. Thus, they would not harm the aquatic life and would not increase the salinity of the water. Recently, the sodium edate (EDTA) [27] and Trisodium NTA [28] have been studied as the replacement of existing inorganic salt for the dyeing of cotton fiber with reactive dyes.

8. Conclusions

It may be summed up from this review that cotton is one of the prominent fibers used mostly. The reactive dye is mostly used for the dyeing of cotton, which can be bonded with cotton fabric by two mechanisms mentioned above. The cotton can be dyed by both exhaust and continuous methods. The main problem of cotton dyeing industry is the water pollution obtained in the result of dyeing of cotton. Recently, various strategies have been made to overcome this problem. These strategies include changes in the dye structure, changes in dyeing machinery, chemical modification of cotton fabric and use of eco-friendly auxiliaries in the dyeing of cotton.

Conflict of interest

The authors declare that there is no conflict of interest.

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