

Review Article

Cationic Modification of Cotton for Salt-free Reactive Dyeing: A Review

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Abstract

Cotton is still the king of fibres, and most of world's apparel is made of cotton due to its unique comfort, good dyeability, ease of production, biodegradability, and relatively low cost. To satisfy consumers aesthetically, cotton products, like garments and household textiles, must have a large color gamut and satisfactory fastness. The most popular dyes for dyeing cotton are the reactive dyes because of their brightness of shade, wide colour gamut, flexible application procedures and all-round good colour fastness properties of the resultant dyeing's. In recent years, reactive dyes maintain the largest annual consumption in the world among the dyes used for cotton dyeing. But some problems, such as low dye utilization, large amount of electrolyte used and high volume of wastewater discharged, always exist in the application of reactive dyes. With growing popularity of reactive dyes for dyeing of cotton, environmental problems associated with their use have received attention. Cotton acquires negative charge in aqueous medium and thus repels negatively charged dye anion during dyeing. Such repulsion between fibre and dye is offset by using large quantity of salt in dye bath, particularly for reactive dyes. A low dye bath exhaustion also leads to low dye fixation of reactive dyes on cotton. Thus, the use of high salt concentration and low reactive dye fixation lead to environmental problems related to highly coloured effluent with high salt content. Hence, modifying the cotton fibre to increase dye-fibre interaction is therefore the best route to overcome the lack of affinity for cotton to reactive dyes making salt-free reactive dyeing. However, majority of the chemicals used for imparting cationic sites in cotton are themselves not ecofriendly.

Keywords: Cotton; Cationization; Cationic agents; Salt Free Dyeing; Reactive dyes.

Introduction

In industrial process, reactive dye was widely used for cotton fabric dyeing, it has wide color gamut, producing brilliant and high wet fastness [1,2]. Reactive dyes stand out from other dyes by their ability to make covalent bonds between carbon atoms of dye reactive group and oxygen atoms of cotton hydroxyl groups under alkaline conditions. When cotton come in contact with water produce slightly negative charge due to the ionization of hydroxyl groups, whereas most of the dye classes suitable for cotton are anionic in solution. The slightly negative charge on the fibre results in the repulsion of anionic dyestuffs and thus the exhaustion of the bath is limited. However, by adding an electrolyte like sodium chloride or sodium sulphate, the charge repulsion factor can be offset and thus increased dye exhaustion is achieved. The reactive dyes, in particular,

require large quantities of electrolyte for its exhaust application, leading to environmental problems. In addition, inadequate dye bath exhaustion and dye fixation pose the problem of color effluents. Therefore; a dyeing procedure leading to high dye fixation could be of great benefit to minimize the environmental problems [3-8].

The dyeing of one kilogram of cotton with reactive dyes demands from 70 to 150 litre water, 0.6-0.8 kg NaCl and from 30 to 60 g dyestuffs. More than 80,000 tons of reactive dyes are produced and consumed each year [9, 10]. These electrolytes are neither exhausted nor destroyed and hence remain in the discharge dye liquor which leads to enormous environmental problems. Apart from this, only 60-65% dye utilization is attainable even with the use of salt in the normal dyeing system. Due to these problems this class of dyes is the most

unfavorable one from the ecological point of view, these effluents produced gives high values of BOD/COD (Biological oxygen demand /Chemical oxygen demand) and increases salinity of the rivers affects the delicate biochemistry of aquatic life [10-13].

In the textile industry, ecology and economy are the two important aspects in the today's worldwide scenario. This demands the minimization of pollution load for the textile effluents, particularly in the dye-houses. With advantages in wet fastness properties and a wide range of hue, reactive dyes are one of the most commonly used dyes for cotton coloration. However, the conventional reactive dyeing process is plagued with a high degree of salt utilization and colored effluent due to unexhausted, unfixed, and hydrolyzed dyestuffs. This is caused by the same anionic charges of both reactive dyes and cotton in water, resulting in poor affinity of most reactive dyes for cotton. With the need for cleaner, cost-effective, and colorfast textile products, innovative technologies and improved processes have been developed for cotton coloration. As an important root to obtaining the desired dyeing performance with existing dyes, chemical modification of cotton fiber to impart cationic charges have been widely researched in recent years. By introducing cationic groups into cotton fibers, the affinity of anionic dyes for cotton was significantly improved, which allows the dyeing of cotton fabrics without salt and to improve reactive dye utilization. With less chemical, water, and energy consumption, the dyeing of cationized cotton is a potentially environmentally responsible process [5,6,13,14].

Chemical modification of cotton has been earlier studied by many researchers in different ways and means, which are widely available in the literature. Majority of the chemicals used for introducing cationic sites in cotton are themselves not safe environmentally [4,6]. However, these problems can also be overcome by improving the dye substantivity of cotton in the absence of salt or with low salt additions. One such approach is cationization of cotton which is critically explored in this investigation. The present investigation will attempt the pretreatment of cotton before dyeing can offer a simple and effective method of improving dye-fiber affinity, avoiding the need for salt as an electrolyte in the dye bath [15]. Nowadays, the

recent trend is to carry out eco-friendly chemical processing using natural products, if possible, for the need to strike a balance between textile properties and dyeability of the textile material. Many researchers considered as cationization of cotton using natural waste product is a sustainable alternative approach to the conventional reactive dyeing of cotton. However, cationization using synthetic agent is not sustainable alternative, as the chemicals are non- biodegradable, toxic and expensive.

Cotton fiber

Cellulosic fibers are significantly dominated by cotton. It is a polymer of high molecular weight consisting of long chains of D-glucose units connected by β -1, 4- glucosidic bonds as shown in fig. 1 and consequently may be considered as a polyhydric alcohol [16,17]. Each glucopyranose ring on the cellulose chain contains three hydroxyl groups, a primary hydroxyl group in the 6 position and secondary hydroxyl groups in the 2 and 3 positions. The primary alcohol is more easily neutralized and readily available and prominent in chemical reactions of cellulose [14].

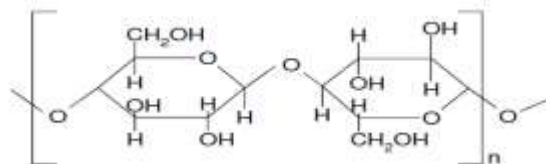


Fig. 1. Chemical structure of cellulose

The dissociation constant for cellulose refers to the ionization of the hydroxyl group in the 6 position of the glucopyranose ring. The hydroxyl groups in positions 2 and 3 of the ring are less acidic. Therefore, cellulose is ionized under alkaline conditions and can behave as a nucleophile towards compounds containing electron deficient carbon atoms (e.g. reactive dyes) [13].

Fiber reactive dye

Reactive dyes are the most widely used dyes for dyeing cotton substrate. Reactive dyes stand out from other dyes by their ability to make covalent bonds between carbon atoms of dye reactive group and oxygen atoms of cotton hydroxyl groups under alkaline conditions [10, 18]. The reactive dyes offer a wide range of dyes with varying shades, fastness, cost with high brilliancy, easy applicability and reproducibility [13,18,19].

Reactive dyes are best as they can be applied by various methods and give better fastness properties. The exhaustion of the dye onto the fiber requires large quantity of salt. The salt used is not exhausted onto the fiber and remains in the dye-bath. Also the dye exhaustion onto the fiber is only around 60% to 70%. The left over unexhausted dye solution is discharged as effluent, thereby polluting the environment [11, 17,18].

General structure of reactive dyes

A typical structure of reactive dye molecules contains a chromogen (C), solubilizing groups (S), a bridging group (B), and a reactive group (R) with leaving groups (L).

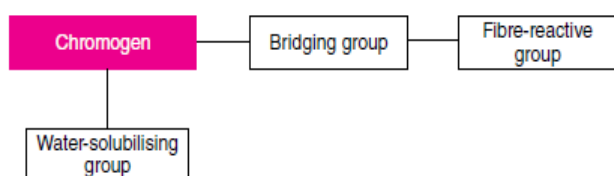


Fig. 2. General structure of a fibre-reactive dye

The chromogen is a conjugated system containing one or more chromophores which provides the color to the dye. The reactive group is capable of reacting with the hydroxyl groups on cellulose by addition or substitution reactions. In between the two functional groups, a bridge group connects but also insulates the chromogen from the reactive group to prevent the color generated by the chromogen from changing. Solubilizing groups provide characteristics such as water solubility, substantivity, migration and wash-off. The dominant solubilizing group in reactive dyes is the sulphonic substituent [6, 13,14].

Chemistry of reactive dyes

The introduction of reactive dyes for Cellulose in 1956 was the most important event in the history of reactive dyeing. As one of the first invented reactive dyes, Reactive Orange 1 in Fig. 3 has the dichlorotriazine (DCT) as its reactive group [6, 20]. Reactive dyes are divided, according to the structure of reactive group, in haloheterocycle and vinyl sulfone based dyes, which react with cellulose through nucleophilic substitution and addition mechanisms, respectively [14,18]. First for the halogenic heterocyclic derivatives (such as DCT), the reaction mechanism with cellulose is a nucleophilic substitution (Fig. 4) of a labile chlorine, fluorine, or nicotinyl leaving group

activated by an adjacent nitrogen atom in the heterocyclic ring. On the other hand, the vinyl sulfone group reacts with cellulose by nucleophilic addition to the carbon-carbon double bond activated by the adjacent electron-attracting sulfone group. As shown in Fig. 5, the vinyl sulfone is not present in the dye molecule initially and should be generated in the dye bath by elimination of sulfate ion from a sulfatoethylsulfone group under basic conditions [13,14,20].

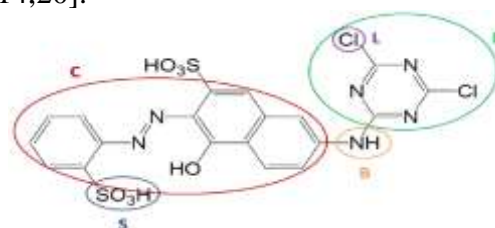


Fig. 3. Typical structure of a fiber reactive dye: C.I. Reactive Orange 1

Fig. 4 and 5 shows competing reactions of a DCT and VS type reactive dyes. For both reaction mechanisms, alkaline conditions are required to enable the reaction and there are competing hydrolysis reactions of the dye. Thus, many reactive dyes applied with exhaustion methods, especially with high liquor ratio, have relatively low fixation rates. To obtain a higher fixation rate, many of the newer reactive dyes have more than one reactive group. Those bifunctional reactive dyes can have two identical or different reactive groups in the dye molecule [13,20].

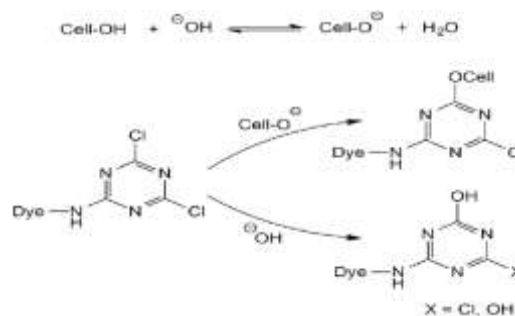


Fig. 4. Nucleophilic substitution reactions of DCT type reactive dyes

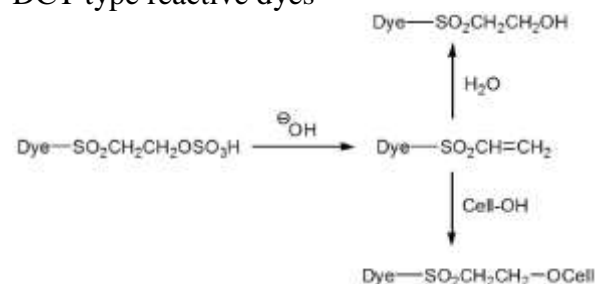


Fig. 5. Nucleophilic addition reactions of VS type reactive dyes

Commercially, the widest used systems are: vinyl sulfone (VS), monochlorotriazine (MCT), bifunctional dyes, difluoro chloropyridine (DFCP), monofluorotriazine (MFT) and dichlorotriazine (DCT) [18].

Problems in dyeing with reactive dyes

Cotton and regenerated cellulosic fibers can be dyed with various classes of dyes. Most prominently, reactive dyes are widely employed for dyeing cellulose fibers because of their brilliance, wide shade gamut, and excellent fastness properties [10,11,18,19]. Dyeing of cellulose fibers with reactive dyes still suffers from two major disadvantages; one is poor dye uptake and other one is unsatisfactory dye fixation, both of which lead to environmental pollution. Poor dye uptake is related to the existence of the charge barrier effect between the negatively charged fiber surface and anionic reactive dyes. This problem can be solved by adding a large amount of electrolytes, to the dye bath in order to suppress the negative charge on the fiber surface and then allowing reactive dye molecules to diffuse inside the fiber. In the case of poor dye fixation, the contributing factor is the presence of inactive hydrolyzed dye. Since fixation of reactive dyes onto cellulose fibers requires alkaline dyeing conditions in order to activate the hydroxyl group of cellulose to be able to react with the dye, some of the reactive dye can inevitably undergo the competing hydrolysis reaction with hydroxide nucleophiles, resulting in a reduction in the efficiency of the reaction with the cellulose substrate [4,10,15,19-21]. Reactive dyes also have some drawbacks: fair light fastness, low chlorine resistance, relatively high cost and low reaction efficiency. Due to the competing hydrolysis reaction of the reactive dyes, dye fixation efficiency on cellulosic fiber is generally low [6].

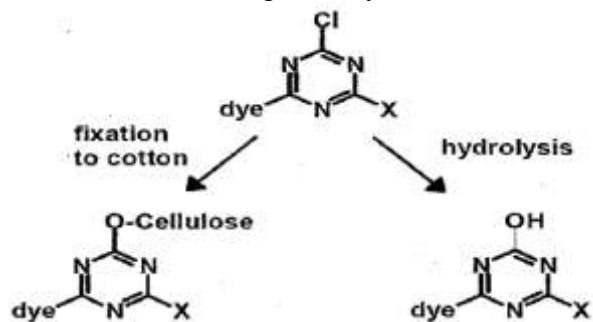


Fig. 6. Reaction of a reactive dye with cotton fibre and water

Environmental problems associated with reactive dyes

Due to the poor affinity and limited reaction efficiency of reactive dyes, there are high concentrations of dye and electrolyte remain in the wastewater when reactive dyes are applied on cotton in conventional dyeing processes, which causes serious environmental problems. Also, substantial level of unfixed and hydrolyzed dyes on fiber requires heavy water consumption for multiple soaping and rinsing [6].

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. If a textile mill discharges the waste water into the local environment without any treatment, it will have a serious impact on natural water bodies and land in the surrounding area [22]. Reactive dyeing thus pollutes the environment by discharging highly colored reactive dye bath and higher electrolyte concentration.

Impact of salt

The molecules of reactive dyes are smaller than those of direct dyes, and their smaller size is accompanied by a correspondingly lower substantivity. Cotton builds up negative charges on its surface when immersed in water, results an inverse effect on exhaustion of anionic dyes. The negative surface charge of textile fibers, known as zeta potential (ζ), hampers anionic dye adsorption on the fiber surface. The slightly negative charge on the fibers repels anionic dyestuff and hence the efficiency of dye exhaustion and fixation on cellulosic fiber is generally low [6,14,15]. As a result, large amount of salt is required to decrease the repulsion of negative-negative charges and thence improves exhaustion [23].

Salt performs two key functions during dyeing of cotton with reactive dyes. Sodium chloride or sodium sulphate is fully dissociated in water to loose ion pairs of sodium (Na^+) and chloride (Cl^-) or Sulphate (SO_4^{2-}) ions. The positive sodium ion has the capability of traveling to the fiber/water interface and effectively negating the zeta potential, destroying the barrier to the initial dye/fiber interaction [5,23].

Picturing the water as a lattice structure that has only limited sites for accommodating charged species, and considering the fact that

dissociated sodium salt is more compatible with the water lattice than a large molecular weight, dye molecule with a few sulphonate groups hanging off, the salt is the preferred species to occupy the limited lattice sites. Dye is thus effectively "salted out" of the bath, with the distribution coefficient of the dye shifted from solution towards the fiber. Both these actions of the salt lead to the reactive dye exhaustions achieved during dyeing of cotton with reactive dyes [5].

The amounts of salt required for exhaustion and the depth of shade for heavy reactive dye formulations lead to large amounts of salt released in the effluent and discharged to streams and rivers. Salt concentrations may be as high as 100 g/L for dark shades. Salt may be considered as one of the most toxic chemicals emitted from textile mills because of the quantity released, albeit not necessarily the toxicity of the salt itself. Finally, if the effluent must be treated, i.e. desalinated, the additional cost of this processing step makes the desalination unattractive just from an economical point of view [14].

Higher electrolyte concentration in the effluent causes worst effect such as impairing the delicate biochemistry of aquatic organism, destructive attack on pipes if sodium sulphate is used as electrolyte due to the formation of alumino sulphato complexes which swell and crack concretes with considerable alumina content, evolution of hydrogen sulphide gas under anaerobic conditions when sodium sulphate is used as electrolyte, dissolution of such sulfides and subsequent bacterial oxidation to be harmful sulphuric acid and leading to higher Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Dissolved Solids (TDS) [11,12].

Impact of alkali

Most all reactive dyes require alkali to be added to the reactive dye bath in order to facilitate bonding of cellulose with the reactive dyestuffs. As a result, large amounts of alkaline dye bath solutions are dumped directly into the effluent [5,14]. In some cases, the fabric is never neutralized and neutralization may only be required in the case of VS dyes. Depending on the reactive chemistry being used, the reactive dye may be very reactive at low temperatures with low amounts of a milder base such as

sodium carbonate for DCT dyes, or requiring sodium hydroxide for VS type dyestuffs [14].

Colored effluent

Another major polluting factor of reactive dye coloration of cotton is the significant amount of color pollution as a result of dye hydrolysis [14].

Dye fixation efficiency of reactive dyes on cellulosic fibers is generally low (varying from 50-90 %). This, results in a highly colored dye effluent, which is unfavorable on environmental grounds [23]. Simultaneously, with the reaction of the dye with cellulose, a certain amount of the dye also reacts with water, thereby removing the particular reactive group from the dyes [9]. When this happens, the dye is said to be hydrolyzed. The unfortunate feature of the reactive dye is that a certain amount of unfixed hydrolyzed dye is retained on the fibre. It is necessary to remove unfixed dye [22].

Unfixed reactive dyes and/or hydrolyzed dye along with alkali used for fixation may pose an environmental hazard because the hydrolyzed dye will pass in the effluent, thereby increasing the pollution load. Certain reactive dyes, like mono and dichlorotriazine or fluorotriazine type of dyes may cause the passage of organohalogens in the discharge effluent, which may by-pass the permissible discharge limits fixed by certain countries.

Water usage

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater. Due to the hydrolysis of the dye, the dyeing effluent consists of a large amount of hydrolysed dye, and it requires a high volume of water to remove the hydrolysed dye in a wash-off process. This wastewater therefore contains a significant quantity of dye and salt, leading to serious environmental problems [15].

Additionally, the amount of water usage and time required to adequately rinse and remove hydrolyzed reactive dye cause the entire dyeing process to be greatly extended. Finally, it is common practice to utilize soaping aids in the removal of hydrolysate, but it has been reported that these soaps do little to improve fastness of the dyed goods but greatly increase organic pollution in the effluent [6].

The textile dyeing wastewater has a large amount of complex components with high

concentrations of organic, high-color and changing greatly characteristics. Owing to their high BOD/COD, their coloration and their salt load, the wastewater resulting from dyeing cotton with reactive dyes are seriously polluted. As aquatic organisms need light in order to develop, any deficit in this respect caused by colored water leads to an imbalance of the ecosystem [9].

Major development in cotton coloration

Major developments in environment-friendly dyeing of cotton with reactive dyes are in terms of innovations in dyes and dyeing processes for high dye bath exhaustion and fixation, use of low-salt reactive dyes, machinery developments for dyeing at low liquor ratio, pad troughs with reduced volumes, replacement of chemicals, econtrol process etc are some of the approaches for ecofriendly colouration of cotton with reactive dyes [24].

With the need for cleaner, cost-effective, and colorfast textile products, innovative technologies and improved processes have been developed for cotton coloration. The innovations mainly focused on three aspects:

- 1) Development of new dyes and auxiliaries;
- 2) Developments in dyeing machinery and processes;
- 3) Chemical modifications of cotton fiber prior to dyeing [13, 25].

Developments in dye structure

With the unique dye structure and application mechanism, much attention from both industry and research has been focused on the development of reactive dyes. To increase the fixation efficiency and reduce chemical waste, reactive dyes with two or more reactive groups have been developed and commercialized. The bifunctional reactive dyes, including homobifunctional dyes (containing two identical reactive groups, e.g. the Procion H-E dyes) and heterobifunctional dyes (containing two different reactive groups, e.g. the Everzol dyes), were already widely used in industry [26]. There are also successful commercial trifunctional reactive dyes such as the Avitera SE dyes from Huntsman which are claimed to save energy and time and reduce water consumption [27]. Researchers also came up with some polyfunctional reactive dyes with

more than three reactive groups, but none of them have been commercially applied yet [28-30]. A typical example is the reddish-grey to black chromium complex (Fig. 7) patented by Hoechst. The drawbacks with more reactive groups include higher cost and lower color strength. The extra reactive groups “dilute” the color value of a dye by increasing the molecular weight of the dye but do not enhance chromogenic strength [31].

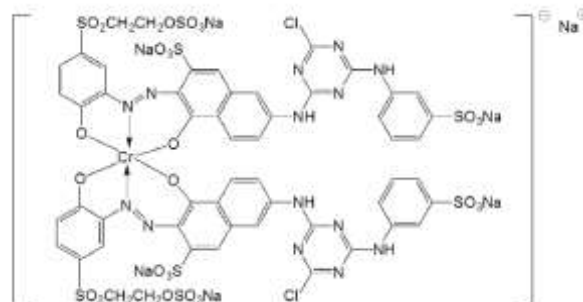


Fig.7. Reddish-grey to black chromium complex

Besides the increase in reactive groups, other innovations on reactive dyes include high strength economic chromophores, high light fastness chromophores [26], neutral-fixing [32, 33], or acid-fixing reactive dyes [34], and cationic reactive dyes [35-37].

Developments in dyeing machinery and processes

To reduce the chemical, water, and energy consumption in exhaust dyeing, a wide number of low liquor-to-fiber ratio dyeing machines have been developed [38-40] such as the Luft-roto Plus dyeing machine from Thies with the minimum liquor ratio as 4:1 [41,42]. While for pad dyeing, new padders and low capacity padding troughs were designed to reduce liquor waste and eliminate tailing [39, 40]. Also, the Econtrol dyeing process developed jointly by BASF and Monforts eliminates the use of urea and salt for continuous dyeing of cellulosic fibers [43]. While for washing-off, new approaches such as the “enzymatic after soaping” process for exhaust dyeing were announced for water and energy savings.

Other emerging technologies on cellulosic dyeing include the use of ultrasonic energy, microwave heating, and supercritical carbon dioxide (scCO₂). The studies on ultrasonic-assisted cotton coloration shown that the use of ultrasound can result in better color yield and savings in energy, water, time, and chemical [49-53]. Compared with the

conventional heating method, microwave is a volumetric heating which can shorten the heating time for coloration at the same time of improving color yield and dye fixation efficiency [44, 45]. In another aspect, cotton can be dyed with disperse reactive dyes in $scCO_2$, which eliminates the use of water [46]. Also, cotton modified to be less hydrophilic can be dyed with disperse dyes in $scCO_2$ [47, 48].

Modification of cotton fiber prior to dyeing

Synthesis of new dyes and modification of cotton dyeing processes, while valid for obtaining qualified black cotton dyeing, are likely to involve significant capital investment and development costs [54]. Thus, much attention has focused on modification of cotton fiber as another route to obtaining the desired dyeing performance and fastness properties with existing dyes and processes. Cationization of cotton is one of the most widely researched modifications in recent years since both direct and reactive dyes carry anionic charges and they exhibit high affinity for positively charged cotton. Numerous chemicals and methods have been used to introduce cationic groups into cotton fiber [6, 13].

Cationization of cotton

The process of modifying cotton by developing cation site on its surface without affecting its bulk property is called 'cationization'. Modifying the cotton fibre to increase dye-fibre interactions is thus, best route to overcome the lack of affinity for cotton to commercial reactive dyes, so that it can be dyed without salt. It was found that during cationization of cotton, etherification of primary hydroxyl groups on cellulose takes place [55, 56].

The introduction of cationic sites within the cellulose is the most expected technique to increase the dye adsorption. Cationic sites can be introduced either by aminization or cationization. Cationization is one of the most important modifications for cellulose. The cationization is mainly carried out to improve affinity toward anionic substances, such as dyes in conventional textile processing and metal ions or unfixed dyes in effluent treatment. Cationic modification is the method that has been employed in order to change the surface charge of cellulosic fibers [16, 21].

Cellulosic materials are commonly cationized in three ways: firstly, a direct cationization of cellulose using a chemical compound with suitable functional groups that react with cellulose hydroxyl groups. The second approach involves the addition of binding agent, such as dimethyloldihydroxyethylene urea (DMDHEU), which reacts both with cellulose hydroxyl and the functional group of cationic agent. This process is mainly used for textile application since the common textile pad-dry-cure process can be employed. The third approach utilizes graft polymerization to introduce monomeric or polymeric cationizing agents within the cellulose, but it is not commercially applicable. Each process has advantages and disadvantages, but none of these processes has been commercially adopted yet [16].

Reasons for cationization

As previously mentioned, cellulose is the major component of cotton. While in contact with water, negative charges build up on the surface of cotton due to the partial ionization of hydroxyl groups on cellulose. Thus, cotton fibers have electrostatic repulsion to reactive and direct dyes, which are sulfonated and negatively charged. Anionic dyes have to overcome a significant adverse charge barrier before they are adsorbed on cotton fibers [67]. High concentrations of electrolytes, such as sodium chloride and sodium sulfate, are used in the conventional dyeing procedure of cotton with reactive dyes to suppress the negative charge build-up and reduce the solubility of dyes. Even with electrolytes added, the fixation rate of reactive dyes is still relatively low, especially when high concentrations of dyes are applied. As a result, the dye bath wastewater typically contains high concentrations of both salt and unexhausted dye, which causes serious environmental problems.

By introduction of cationic groups into cotton fibers, the affinity of reactive dyes for cotton can be significantly improved. The ionic attractions between cationized cotton and reactive dyes can result in increased dye uptake, reduced or no electrolyte use, less dye washing off and less water and energy consumption. The environmental problems caused by dye and salt in effluent can be potentially mitigated by cationization pretreatment of cotton [6, 13].

Cationic reagents

Many researches worked to use variety of cationic compounds in order to improve the dyeability of cotton fabrics toward reactive dyes. A number of processes have been proposed from early 1930s till date, to improve the substantivity of anionic dyes towards cellulosic fibres by introducing cationic sites in the fibres. *Schlack (1938)* was the first to report improved affinity of acid dyes towards cellulose, modified through the introduction of epoxy derivatives [57]. *Clampetier et al. and Merle* modified cellulose by a reactions epoxy diethylamine-3-propane followed by an ethyl iodide quaternization and reported the dyeing the dyeability of modified cellulose towards acid dyes [58, 59]. *Rupin (1976) and Rupin et al. (1970)* studied the dyeability of cellulose towards direct and reactive dyes after pretreatment with glycidyltrimethyl ammonium chloride (Glytac) and simultaneous modification and dyeing by exhaust, pad-batch and pad-cure processes [60, 61].

Glytac-pretreated cellulose showed improved dyeability in exhaust application, towards reactive dyes in the presence of alkali and salt. Pretreatment of cotton with polyamide epichlorohydrin type polymer, offers the opportunity for increasing both the substantivity and reactivity of cotton towards reactive dyes under neutral to acidic condition due to the introduction of cationic azetidinium group [62]. *Wu and Chen (1992)* treated cotton with poly epichlorohydrin (PECH) dimethylamine which was manufactured by initial polymerization of epichlorohydrin, followed by amination with dimethylamine [63].

The epichlorohydrin was polymerized in carbon tetrachloride using boron trifluoride etherate as catalyst. The dyeability of treated cotton towards direct dyes was investigated and it was found that PECH-amine could improve the direct dyeability of modified cotton. In another work they have reported (*Wu and Chen, 1993*) the effect of PECH-amine treatment on the reactive dyeability of cotton. It was found that the modified cotton can be dyed with selected low reactivity dyes under neutral condition using limited salt concentrations or with selected high reactivity dyes without salt [64].

The effect of modification of cotton using various N-ethylolacrylamide derivatives,

viz. bis(N-methylol-2-cabamoylethyl)butylamine, N-(N,N'-dimethylol-2-cabamoylethyl) diethylamine and N-(N, N'-dimethylol-2-cabamoylethyl) dimethylamine on acid dyeability has been investigated by [65]. These agents were applied to cotton fabric by pad-dry-cure procedure. Such treatments were found to improve the crease recovery angle and acid dyeability. But these agents release hazardous formaldehyde during curing as well as on storage [4, 5, 11, 16].

Researchers have investigated different kinds of cationic reagents for the cationization of cotton. Based on the molecular weight; the cationic reagents can be divided into two groups, monomeric reagents and polymeric reagents. Epoxy compounds, chlorotriazine type quaternary compounds, N-methylolacrylamide, choline chloride etc. are the monomers commonly used in modification of cotton fiber.

Synthetic polymers polyepichlorohydrin dimethylamine, polyamide epichlorohydrin type polymers, poly-(4-vinylpyridine) quaternary ammonium compounds and dendritic polymers, and biopolymers-chitosan, starch and their derivatives are typical compounds commonly used in modification of cotton [3, 6, 66].

Researchers have investigated different kinds of cationic reagents for the cationization of cotton. Both chemical and physical modifications of cotton with compounds including monomers and polymers were employed. Epoxy compounds, chlorotriazine type quaternary compounds, N-methylolacrylamide, choline chlorides etc. are the monomers commonly used in modification of cotton fiber. Synthetic polymers, polyepichlorohydrin dimethylamine, polyamide epichlorohydrin type polymers, poly-(4-vinylpyridine) quaternary ammonium compounds and dendritic polymers, and biopolymers-chitosan, starch and their derivatives are typical compounds used in modification of cotton [3,6,13,66].

All agents used for cationization, both monomeric and polymeric, have their limitations, but generally speaking, the more complicated the reagent, the more synthesis steps are required resulting in high costs for the reagents. Additionally, vinyl reagents must be free radical polymerized in situ with an initiator. Finally, reagents such as choline chloride with

no reactive group require a cross linker such as DMDHEU and the complications associated with cross linking such as formaldehyde release and reduced breaking strength of the treated fabric. Moreover, all the above chemicals are non-biodegradable as well as non-renewable [6, 14].

Different approaches, such as modification of the dye structure to make it more substantive to cellulose, cationization of cellulose through chemical reaction with compounds containing cationic groups or controlled dosing of dye and salt during the exhaustion process, have been recommended to control the above mentioned effluent problem [4, 13]. Most of the techniques developed so far for reducing salt concentration in cotton dyeing are complicated in nature. Some of these methods are successful only for highly reactive dyes. Under this background, efforts were made to find out easier method for salt free reactive dyeing of cotton [5].

Currently, there is a growing interest in the development of biodegradable cationizing agent in keeping with the requests of people for environmental protection. In terms of environmental friendliness, cost, and ease of application, using bio product cationizing agent, is without a doubt the method of best choice for cationization of cellulose being biodegradable and renewable.

Dyeing process

An Ahiba Texomat dyeing machine (Fig. 8) was used for the dyeing of both uncationized and cationized cotton samples. A conventional dyeing procedure was used for uncationized cotton fabrics and the no salt dyeing procedure was used for the cationized cotton samples. A liquor ratio of 20:1 was used for all dyeings. Besides the dyes, Na_2SO_4 and Na_2CO_3 were added in the dyeing procedure of uncationized cotton fabrics while only Na_2CO_3 was added in the dyeing procedure of cationized cotton fabrics [6].

Conventional dyeing procedure

- 1) Dissolve Na_2SO_4 in water at room temperature.
- 2) Immerse the rolled fabric into the solution.
- 3) Heat to 30 °C.
- 4) Add dye in 5 minutes at 30 °C.
- 5) Hold at 30 °C for 5 minutes.

- 6) Add half of the Na_2CO_3 in 5 minutes at 30 °C.
- 7) Hold at 30 °C for 5 minutes.
- 8) Heat to 60°C at 1.0°C/min.
- 9) Add the other half of Na_2CO_3 in 5 minutes at 60 °C.
- 10) Hold at 60 °C for 25 minutes.
- 11) Cool to 40 °C then discard bath.
- 12) Wash and rinse manually for 10 minutes with room temperature water.
- 13) Neutralize with citric acid.
- 14) Wash and rinse manually for 10 minutes with room temperature water.
- 15) Extract fabric and dry.



Fig. 8. Ahiba Texomat dyeing machine

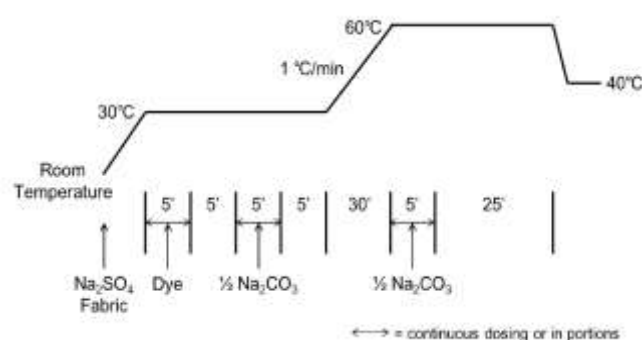


Fig. 9. Conventional dyeing procedure

No salt dyeing procedure

- 1) Dissolve dyes in water at room temperature.
- 2) Immerse the rolled fabric into the solution.
- 3) Heat to 30 °C.
- 4) Add Na_2CO_3 in 5 minutes at 30 °C.
- 5) Hold at 30 °C for 5 minutes.
- 6) Heat to 60°C at 1.0°C/min.
- 7) Hold at 60 °C for 30 minutes.
- 8) Cool to 40 °C then discard bath.
- 9) Wash and rinse manually for 10 minutes with room temperature water.
- 10) Neutralize with citric acid.
- 11) Wash and rinse manually for 10 minutes with room temperature water.
- 12) Extract fabric and dry

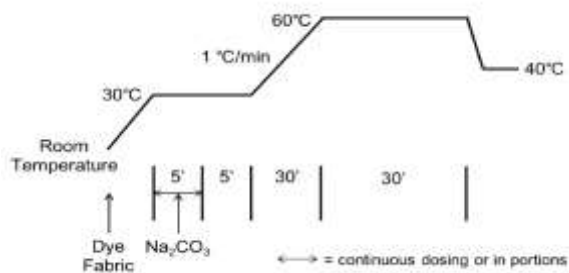


Fig. 10. No salt dyeing procedure

Conclusion

The conventional reactive dyeing process is plagued with a high degree of salt utilization and colored effluent due to unexhausted, unfixed, and hydrolyzed dyestuffs. This is caused by the same anionic charges of both reactive dyes and cotton in water, resulting in poor affinity of most reactive dyes for cotton. With the need for cleaner, cost-effective, and colorfast textile products, innovative technologies and improved processes have been developed for cotton coloration. As an important root to obtaining the desired dyeing performance with existing dyes, chemical modification of cotton fiber to impart cationic charges have been widely researched in recent years. An alternative and environmentally attractive approach to cotton dyeing is through cotton modification rendering cotton with a permanent positive charge. By introducing cationic groups into cotton fibers, the affinity of anionic dyes for cotton was significantly improved, which allows the dyeing of cotton fabrics without salt and up to 100% reactive dye utilization. The permanent positive charge allows the uptake of suitable anionic dyestuffs without the need for salt and with sustainable environmental and financial savings. With less chemical, water, and energy consumption, the dyeing of cationized cotton is a potentially environmentally responsible process. Moreover, the cationic dyeing process greatly reduced, the amount of water usage and time required to adequately rinse and remove hydrolyzed reactive dye. So, a significant savings in process costs was also achieved from the cationized cotton dyeing method. Instead of focusing on synthesis of new dyes and modification of cotton dyeing process, much research has focused on modification of cotton at the molecular level to obtain the desired dyeing performance and colorfastness properties with existing dyes. In all well-studied modifications of cotton, cationization has been shown to be effective in

increasing the dye uptake of anionic dyes. Furthermore, it allows salt free dyeing with anionic dyes.

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Conflicts of interest

The author declares no conflict of interest.

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