The Influence of Cationization on the Dyeing Performance of Cotton Fabrics with Direct Dyes

M. F. Shahin
Textile Printing, Dyeing & Finishing Dept., Faculty of Applied Arts, Helwan University, Giza, Egypt.

Abstract
The effect of cationic modification of cotton fabrics, using cationic agent (Chromatech 9414) on direct dyeing characteristics was studied in this work. Cationization of cotton fabric at different conditions (pH, cationic agent concentration, temperature and time) was investigated and the optimum conditions were determined. Nitrogen content of cotton samples pretreated with cationic agent was indicated. The results showed that increasing cationic agent concentration lead to higher nitrogen content on cotton fabric. The cationized cotton fabrics were dyed with two direct dyes (C.I. Direct Yellow 142 - C.I. Direct red 224) and the results were compared to untreated cotton fabrics. The parameters which may affect the dyeing process such as dye concn., addition of salt, time and temperature of dyeing were studied. The dyeing results illustrate that cationization improves the fabric dyeability compared to the uncationized cotton and the magnitude of increase in colour depth depends on the nitrogen content of the cationized cotton fabric. The results also refer to possibility of dyeing cationized cotton fabric with direct dyes without addition of electrolytes to give colour strength higher than that achieved on uncationized cotton using conventional dyeing method. Another important advantage of cationic treatment is in the saving of dye concn., energy, dyeing time, rinse water and subsequently saving of waste water treatment, and finally minimizes the environmental pollution. The changes in surface morphology of fibres after cationization were identified by various methods such as wettability and scanning with the electron microscope. Different fastness properties were evaluated.

Key words: Cationization, Dyeability, Direct dye, Nitrogen content, Wettability, Surface morphology.

I. Introduction
Cotton is a natural cellulosic fiber. The polymer chain of cotton consists of several hundreds to more than thousand $\beta(1-4)$ D-glucose units linked to each other. It builds up negative charges on its surface when immersed in water, resulting in an inverse effect on exhaustion of anion dyes. The negative surface charge of textile fibers, known as zeta potential ($\zeta$), hampers anionic dye adsorption on the fiber surface. The slightly negative charge on the fibers repels anionic dyestuff and hence the efficacy of dye exhaustion and fixation on cellulosic fiber is generally low. Many attempts have aimed to improve dye bonding and dye adsorption on materials through chemical modification. [3]

The introduction of cationic sites within the cellulose is the most expected technique [4] to increase the dye adsorption. Cationic sites can be introduced either by amination or cationization. [1] 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. [5] Cationic modification is the method that has been employed in order to change the surface charge of cellulosic fibers. [6-9]

The pretreatment to improve functionality and dyeing ability of cellulose fibers, using cationic agents, has attracted attention recently. [10-13] The reason for such treatment is improvement of cationic activities of cellulose fibers and reduction of electrostatic repulsion of negative ions resulting in a positive effect on absorption of anionic dyes and poly electrolytes. [14] Using commercial cationic agents in the pretreatment of cotton may enhance dye absorption and can not only increase the dyeing color strength but also improve wash fastness. [15] Actually cationization of cotton fabrics is an effective way to reduce the pollution. [16,17]

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 dimethylolhydroxyethylene urea, 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. [5]

Direct dyes are used on cellulose fibers such as cotton, rayon, and linen. The name “direct dye” alludes to the fact that these dyes do not require any form of “fixing”. They are almost azo dyes. They also have sulphonate functionality, but in this case, it is only to improve solubility of the dye. The advantages of direct dyes are resistance to fading in the light and easy to handle. [3]

Pre-treatment of cotton fabrics with mono- and bis-reactive cationic agents produces a fibre that may be dyed with direct dyes under neutral conditions in the absence of salt was studied. [18]

Many researches worked to using variety of cationic compounds in order to improve the ability of cotton fabrics toward direct dyes. [19–21]

The aim of this work is to study the effect of surface modification of cotton fabric with cationic agent (Chromatech 9414) on the dyeability of cotton, as well as the dyeing parameters with direct dyes compared to uncationized fabric, taking into consideration the cost of dyeing and the pollution problems.

II. Experimental

2-1 Materials:

2-1-1 Fabric:
Cotton fabric mill scoured and bleached (160 g/m²) was kindly supplied by Misr Helwan Co. for Spinning and Weaving Helwan, Egypt.

2-1-2 Dyes:
Direct dyes under trade name of Moderdirect produced by Modern Dyestuff & Pigments Co., Tailand, were used throughout this study:

1- Moderdirect Yellow PG (C.I. Direct Yellow 142).
2- Moderdirect Scarlet F2G (C.I. Direct Red 224).

2-1-3 Chemicals and Auxiliaries:
Sodium Chloride, Sodium Carbonate and Acetic Acid of laboratory grade were used. Cationic agent (Chromatech 9414) supplied by Chromatech Co., England, nonionic detergent (TEC Wash RGO) supplied by Egyptian Turkish Co. were used throughout this investigation

2-2 Methods:
2-2-1 Cationization of cotton fabrics:
Cotton samples were treated with aqueous solution of (Chromatech 9414) at L.R. 1:100 with different concentrations (0-20% owf), at pH values (4-8), different degrees of temperatures (40-80°C) and for various durations (10-60min.). The treated samples were rinsed with cold water, squeezed and then air-dried.

2-2-2 Dyeing Process:
The cationized cotton as well as uncationized samples were introduced into a dye bath which contains (1-5% owf) dye at 40°C, NaCl (0-20% owf) was added to the dye bath in two portions through 15 min. The pH of the dye bath was adjusted at 8. The temp. of dye bath was then gradually raised to the required temp. (60, 70, 80, 100°C) during 15 min. and the dyeing process was continued for another (20, 30, 40, 60 min.) at liquor ratio 1:100. The dyed samples were washed with 1g/L non-ionic detergent at 70°C for 15 min., then rinsed with water and dried.
The dyeing process is illustrated in Fig. (1)

2.3 Measurements and Testing

2-3-1 Colour measurements:
The dyed samples were subjected to colour measurement by using reflection spectrophotometer model Optimatch 3100, SDL Company England. The colour strength expressed as K/S values was assessed by applying the Kubelka Munk equation:

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

Where K and S are the absorption and scattering coefficient respectively, and R is the reflectance of the dyed fabric.
2-3-2 Determination of nitrogen content percentage:
Nitrogen content of the cationized fabrics was determined according to kjeldahl method [22].

2-3-3 Determination of the wettability:
A standard method for measuring wettability was used to determine the wettability of the cotton samples treated with different concentrations of Chromatech 9414.

2-3-4 Scanning electron microscope analysis:
Fibres samples previously coated with gold in vacuum coating unit were viewed under scanning electron microscope (JE 100 s), at different magnification. Control fabric was also examined for comparison.

2-3-5 Colour fastness:
Fastness properties of dyed samples were tested according to ISO standard methods. The specific tests were: ISO-X12(1987), colour fastness to washing; and ISO 105-E04, colour fastness to perspiration. The dyed samples were subjected to tests, for fastness to light by AATCC test method 16-1993.

III. Results and Discussion

3-1 Effect of Cationic Agent Concentration on Nitrogen Content:
Cotton fibres can be modified by two ways; i.e. surface modification and internal modification. By surface modification the fibre surface becomes more hydrophilic or hydrophobic according to the type of chemicals used.

In the present work "Chromatech 9414" which is a cationic polymer was used to study its efficiency in cationization of cotton for dyeing with anionic dyes (direct dyes).

Chromatech 9414 was produced essentially for cationization of cotton before pigment dyeing without using binder as in the conventional dyeing method.

The influence of concn. of chromatech 9414 on the dyeability of cotton fabric to direct dyeing was investigated at concn. ranging from 5 to 20% owf. The effect of cationic agent concentration on the nitrogen content of cationized cotton fabric is shown in Table (1).

The results show that the increase in concentration of cationic agent leads to an increase in the nitrogen content of cationized cotton fabric according to the formation of cationic sites on their surfaces.

Table (1): Effect of cationic agent concentration on the nitrogen content of the cationized cotton fabrics

<table>
<thead>
<tr>
<th>Cationic agent conc.%</th>
<th>Nitrogen contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.10</td>
</tr>
<tr>
<td>10</td>
<td>0.17</td>
</tr>
<tr>
<td>15</td>
<td>0.23</td>
</tr>
<tr>
<td>20</td>
<td>0.24</td>
</tr>
</tbody>
</table>

3-2 Factors Affect the Cationization of Cotton Fabrics:
Factors which affect the cationization process including cationic agent concn., pH values, temperature and time of treatment were investigated. The colour strength results for all factors are cited in Fig. (2, 3, 4, 5).
Fig. (2) shows the effect of cationization on the colour strength of cotton fabrics dyed with two direct dyes; namely: C.I. Direct Red 224, and C.I. Direct Yellow 142. The results show that the K/S values of the dyed fabrics depend greatly on the nitrogen content (conc. of cationic agent) of the treated fabrics. The K/S increases with increasing the nitrogen content of the cationic cotton fabrics.

The results also illustrate that the cationization improves the cotton dyeability compared to the uncationized fabrics. The improved dyeability of cationized cotton is attributed to the adsorption of cationic agent on fabric surface creating positive centers capable of attracting anionic dyes via electrostatic attraction forces [3, 23].

The magnitude of ionic attraction between anionic dyes and positively charged fabric surface depend essentially on the nitrogen content of the fabric.

Fig. (3) illustrates that the best colour strength of dyed fabrics is observed when cationization is performed at pH 7 while Fig. (4) presents the effect of temperature treatment on the colour strength of dyed cotton fabric with direct dyes where the best colour strength of both colours are observed at 70°C. Fig. (5) shows that the results of colour strength at different treatment time are observed at 60, 30 min. for yellow and red direct dye respectively.

The difference in results in all factors depends on the structure of the dyes used.

3-3 Optimization of Dyeing Conditions
3-3-1 Effect of dye concentration:

To study the relationship between the concn. of direct dyes used and the amount of dye fixed on cotton fibre expressed as colour strength (K/S) on both cationized and untreated fabric, different dye concentration were used ranging from 1 to 5% owf. The results of K/S measurements are plotted in Fig. (6, 7).
The apparent colour yield of the used direct dyes is significantly higher for cationized cotton than the untreated fabric.

The improvement in shade depth is due to the additional substantively produced by the fixed cationic agent on the cotton fabric. The percent increase in colour yield (K/S) of direct dyeing as a result of cationic treatment is formulated in Table (2): Table (2): Effect of cationization on the % increase of K/S (with respect to the untreated cotton)

<table>
<thead>
<tr>
<th>Cationic agent concn. (%)</th>
<th>(% increase in colour strength)</th>
<th>C.I.Direct Red 224</th>
<th>C.I.Direct Yellow 142</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>28.57</td>
<td>35.10</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>31.17</td>
<td>68.42</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>42.86</td>
<td>75.44</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>53.25</td>
<td>73.68</td>
<td></td>
</tr>
</tbody>
</table>

The results of colour strength from Fig. (6,7) and Table (2) refer to the great alteration in fibre dyeability by cationic treatment and it may be concluded from these results that:

A great amount of direct dyes could be reduced for achieving such a required colour shade depth.

For example, a shade depth (K/S=8.3) can be realized by using 1.45% C.I. Direct Red 142 for dyeing cationic cotton instead of 5% for untreated cotton fabric.

A similar finding may be observed for the yellow dye since 1% dye conc. for cationic cotton is sufficient for obtaining the same shade depth (K/S=10) by using 5% dye conc. for dyeing untreated cotton.

It may be concluded from the previous results that since the dye concn. is almost reduced, the amount of rinse water required and the concn. of dye in the waste water are both very low. On the other hand, the reduced dye concn. in the effluent of dyeing will decrease its impact on the environment.

3-3-2 Effect of salt concentration:

Electrolytes play a great role in dyeing cellulosic fabrics with anionic dyes such as direct and reactive, from practical point of view. Additions of electrolytes to the dye bath facilitate the approach of dye molecules to the fibre surface through removal of the electrical repulsion between the negatively charged fibre surface and the anionic direct dyes.

The removal of negative charge on fibre surface may be carried out either by addition of increased amount of electrolytes or by cationic treatment of cotton to introduce a positive charge instead of the negative ones. By cationization an electric attraction forces will be found between fibre and dye anions result in increasing the dye exhaustion without using electrolytes.

Therefore, the rate and amount of dye exhaustion will depend essentially on:

a) The physical forces of attraction only in case of normal cotton.
b) The ionic attraction between fibre and dye in addition to the physical forces; i.e. hydrogen bonding, hydrophobic attraction, in case of cationized cotton fibre.

Cationized and uncationized cotton fabrics are dyed with 2% direct dyes [Direct Yellow 142- Direct Red 224] , using different concentrations of sodium chloride (zero -20% owf) at 100°C for 60 min. to observe its effect on both colour strength, and dyeing behaviour, the results are cited in Fig. (8)
Addition of NaCl to the dye bath results in an appreciable increase in dye uptake of both yellow and red direct dyes. Maximum colour strength is attained by addition of 5% and 20% for yellow and red dyes respectively. A similar dyeing behavior is observed for both cationized and uncationized cotton fabrics since the slope of dye adsorption on the two fabrics was the same irrespective of the obtained colour strength.

The required and suitable amount of electrolytes to complete the exhaustion depend on the nature and structure of the dye itself as in case of two dyes, i.e. yellow and red. The yellow direct dye is found to be very sensitive to the increased amount of electrolytes, i.e. > 5%, which decrease the exhaustion and the obtained K/S owing to the tendency of dye molecules to exist in aggregated form on opposite of the red dye.

**3-3-3 Effect of dyeing temperature:**

Cationized and uncationized cotton fabrics were dyed with 2% owf direct dye, using 5, 20% sodium chloride for C.I.Direct Yellow 142, C.I.Direct Red 224 respectively, at different temperatures varying from 40 to 100°C for 60 min. The colour strength obtained are cited in Fig. (9).

![Fig. (9): Effect of dyeing temperature on the colour strength of the yellow and red dyes for the untreated and treated fabrics with Chromatech 9414](image)

As shown in Fig. (9), by raising the temperature of dye bath the colour strength gradually increase until reach the maximum value at 80°C for yellow dye after which no further increase in colour strength in case of uncationized fabric while there is slightly decrease in case of cationized cotton fabrics.

Cationization is observed to greatly increase the dye uptake at any dyeing temperature. The percent increase in K/S on cationized fabric is found to reach about 78.87% for yellow dye at 80°C and about 62.34% for the red dye at 100°C with respect to untreated cotton. It may be observed from Fig.(9), that while maximum K/S, i.e. 7.7 is realized on uncationized cotton at 100°C in case of red colour, the same value of K/S may be obtained on cationized cotton at 65°C only. A similar trend was noticed with the C.I. Direct Yellow 142, since a shade depth (K/S=11) was obtained at 60°C only in case of cationic cotton while a maximum K/S not exceed 7 at 100°C for untreated cotton. This means that by cationization a lower energy can be used for realizing a certain colour shade i.e. energy saving.

It may be concluded from the previous results that temperature accelerates the dyeing process via:

a-disaggregation of direct dyes in their aqueous medium since most direct dyes exist very largely in the monomolecular state at temperatures near 100°C.

b-increasing the rate of diffusion of dye molecules in the bulk of dyebath which will accelerate the rate and gradient of adsorption on fibre surfaces.

c-enhance the degree of fibre swelling to promote easier penetration inside the fibre.

d-the dynamic equilibrium state of dyeing process may be attained rapidly by raising the temperature as noted with the yellow direct dye.

**3-3-4 Effect of dyeing time:**

Cationized and uncationized cotton fabrics were dyed with direct dye with 5, 20% sodium chloride for C.I.Direct Yellow 142 and C.I.Direct Red 224 respectively, at 80, 100°C for yellow and red dye respectively at different durations (20-60 min.). The results of K/S measurements are illustrated in Fig.(10).
By lasting dyeing time a gradual increase in colour strength is observed for both yellow and red dyes on both cationized and untreated cotton fabrics. Since maximum colour strength is attained after 40 min. dyeing for the red colour after which no substantial increase in K/S is observed on contrast to the red colour which reach its maximum at 60 min.

It may be concluded, from Fig. (10), that cationization accelerates to great extent the rate of exhaustion and thus the obtained colour strength. The K/S after dyeing of cotton for 20 min. only is observed to be higher than that achieved after 60 min. dyeing of untreated cotton for both dyes.

Maximum K/S was obtained at 60 min. for both yellow (7.6) and red (7.7) on untreated cotton, while when dyeing was performed for 20 min. only on cationic cotton the K/S reached about (10.6) and (9.6) for the yellow and red dyes respectively.

3-4 Determination of the Wettability of Cotton Fabrics:

To evaluate the effect of cationic agent on absorbability of cotton fabric, the wettability of the cationized cotton fabric with different concentrations (0-20%) of cationic agent were carried out comparing the results with the blank. The data are illustrated in Table (3).

![Graph: Effect of dyeing time on the colour strength of the yellow and red dyes for the untreated and treated fabrics with Chromatech 9414](image)

**Table (3): Effect of cationic agent concn. on the wettability of cotton fabrics**

<table>
<thead>
<tr>
<th>Cationic agent conc. (%)</th>
<th>Wettability (absorption time of water drop) sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
<td>64</td>
</tr>
<tr>
<td>15</td>
<td>86</td>
</tr>
<tr>
<td>20</td>
<td>96</td>
</tr>
</tbody>
</table>

It is found from the results that the wettability of cotton fabrics decrease as the concentration of cationic agent increase.

On cationically modified cotton fabrics, water retention value is minimally reduced because cationization occurs mainly on primary hydroxyl groups of C-6 atom of cotton cellulose, so certain number of functional groups is blocked for water molecules. Probably, the fabric pore structure is slightly changed, resulting also in slightly reduced water retention values. Very small change of hydrophilicity of cationized samples cannot negatively affect cotton fiber swelling during dyeing. [14]

3-5 Surface Morphology of Cotton Fabrics:

Surface morphology of the untreated and treated samples is investigated by electron microscopy. The SEM micrographs are shown in **Fig. 11(a-b)**. The images demonstrated that a rough surface is formed by in situ deposition of cationic agent on cotton fabric.
3.4 Fastness Properties:

The colour fastness properties of uncationized and cationized cotton fabrics dyed with two direct dyes (1,2) are evaluated in terms of fastness to washing, perspiration and light. The results are tabulated in Table (4).

The fabrics are compared with grey scale to obtain the colour change compared with fabric before testing. Grey scale has scale from 1 to 5 that scale 1 indicates the most color difference and scale 5 means no color difference.

Dyed uncationized and cationized samples with dye 1 show good to very good fastness results for washing, very good to excellent for perspiration and light fastness.

For dyed uncationized and cationized samples with dye 2 fastness properties show results varied from very good to excellent for perspiration and good to very good for washing, and light fastness. From results it can be noticed that the fastness properties of dye 2 is lower than dye 1 for both untreated and treated samples according to the difference in the structure of the two dyes.

**Table (4):** Colour fastness properties of cationized and uncationized cotton fabrics dyed with direct dyes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Washing</th>
<th>Perspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alt. Staining</td>
<td>Acid Staining</td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>Uncationized dyed cotton with dye 1</td>
<td>3-4</td>
<td>2-3</td>
</tr>
<tr>
<td>Cationized dyed cotton with dye 1</td>
<td>3-4</td>
<td>2-3</td>
</tr>
<tr>
<td>Uncationized dyed cotton with dye 2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Cationized dyed cotton with dye 2</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

(*) refers to staining on cotton fibres and (**) refers to staining on wool fibres.
dye1: C.I. Direct Yellow 142
dye2: C.I. Direct Red 224

**IV. Conclusion**

It could be concluded, from this study, that cationization of cotton fabric leads to the following advantages:

- Increasing the dyeability of cotton fabric towards direct dyes, thus increasing the attained colour strength.
- Excluding the use of electrolytes.
- Saving energy and time of dyeing.
- For achieving a required colour depth the amount of dye can be decreased compared with uncationized cotton fabric.

As a result of saving energy, time of dyeing, concentration of both dyes and electrolytes, the cost...
of dyeing and pollution of environment will be reduced to great extent.

References


