Antibacterial Activity of Cationised Cotton Dyed with Some Natural Dyes
Kamel MM, Helmy HM*, Meshaly HM and Abou- Okeil A
Textile Research Division, National Research Centre, Dokki, Cairo, Egypt

Abstract
The present study was taken up as an exploratory study to test if some natural dyes have inherent antimicrobial activity with a view to develop protective clothing using these natural dyes. For enhancing the dyeability of cotton fabric with natural dyes, three cationising agents namely; Monochloro-S-Triazine, Quat 188 and Solfix E were used. Four natural dyes namely; Madder, Logwood, Cutch and Chelidonium majus were tested against common pathogens Escherichia Coli, Staphylococcus aureus, Aspergilus favus and Candida albicans. Chelidonium majus dye was most effective and showed maximum zone of inhibition there by indicating best antimicrobial activity against all the microbes tested. The color yield of dyed samples was evaluated using K/S measurements. The total difference ΔE CIE (L*, a*, b*) was also measured. The dyed samples were tested to washing, acid and alkaline perspiration, dry and wet rubbing and light fastness. The durability of the antibacterial effect of the dyed cotton fabric was measured after 5, 10 and 20 washing cycles.

Keywords: Cotton; Natural dyes; Antimicrobial; Cationisation; Antibacterial; Macromolecules

Introduction
Increasing the global competition in textile industries created several challenges for textile researchers. There has been upsurge in interest in apparel technology all over the world for much demanding functionality of the products like wrinkle resistance, water repellling, fade resistance and resistance to microbial invasion. Among these, development of antimicrobial textile finish is highly indispensable and relevant since garments are in direct contact with human body [1]. Antimicrobial textiles with improved functionality find a variety of applications such as health and hygiene products, specially the garments worn in contact to the skin and many medical applications such as wound dressings, inflectional control and barrier materials. Cotton fabrics provide ideal environment for microbial growth [2]. Several challenges have been created for apparel researchers due to increasing global demand in textile. Therefore, textile finishes with added value particularly for medical cloths are greatly appreciated and there is an increasing demand on global scale. The consumers are aware of hygienic life style and there is a necessity of textile product with antimicrobial properties. Several antimicrobial agents viz., triclosan, quaternary ammonium compounds and recently nano silver are available for textile finishing [3-11]. However, due to their cost and synthetic in nature which creates environmental problems, natural dyes in textile coloration are gaining significant momentum [12]. This new line of interest is due to stringent environmental standards imposed by many countries due to the usage of synthetic dyes which causes allergic reaction and toxicity. The use of natural products such as chitosan [13] and natural dyes [14-16] for antimicrobial finishing of textiles has been widely reported. Other natural herbal products, such as Aloe Vera, tea, tree oil, Eucalyptus oil and leaf extracts, can also be used for this purpose. Greater interest has emerged in the field of apparel technology using natural colorants, on account of their compatibility with deodorizing properties [12]. Comprehensive literature is available on natural dyes obtained from plants [17].

The aim of the present work is to study the effect of natural dyes (Madder, Logwood, Cutch and Chelidonium majus) on the antibacterial properties of cotton fabrics in presence of different cationising agents.

Experimental
Materials
Natural colouring matter: Colouring substance used in this work was extracted from Madder, Logwood, Cutch and Chelidonium plants.

Fabrics: Cotton fabrics, mill-scoured and bleached (130 g/m²) were kindly supplied by Misr El-Beida Dyers Company, Kafr El-Dawar, Alexandria, Egypt.

Methods
Extraction of natural coloring matter: Madder (Table 1a); Logwood (Table 1b); Cutch (Table 1c); and Chelidonium majus (Table 1d) were crushed to the powder form, and then the coloring matter was extracted using (20 g of the powder in 100 ml water) at the boil for one hour. At the end, the solution was filtered off and left to cool down.

Dyeing method:
Dyeing of cotton fabrics: Cotton fabric samples (8.5 g each) were dyed with the natural color matter extracted from Madder, Logwood, Cutch and Chelidonium majus at liquor ratio 1:40. Dyeing was carried out at pH 5.5 using sodium chloride 5 g/L for 60 minutes at 100°C. The fabric samples were entered to the dyeing solution in a water bath at 70°C then raised to 100°C. The fabrics were dyed for 60 minutes and the dyed samples were rinsed with cold water and washed for 30 minutes in a bath containing 3 g/L of non-ionic detergent at 45°C. Finally, the fabrics were rinsed and air dried.

Preparation of Monochloro-S-Triazine (Cationic agent) (Table 2a): Monochloro-S-triazine cationic agent were prepared using a similar method described previously [18]. N-ethyl-2-anilino...
The reaction was continued for further 2 hours at 80°C. Then the treated fabrics were neutralized using 2% acetic acid at 40°C/5 min. The treated fabrics were washed using 3 g/l nonionic detergent at 60°C/30 min, followed by washing with water and finally drying at room temp.

### Cationisation of cotton using Quat 188

The reaction was repeated for 2 hours at 80°C. Then the treated fabrics were neutralized using 2% acetic acid at 40°C/5 min. The treated fabrics were washed using 3 g/l nonionic detergent at 60°C/30 min, followed by washing with water and finally drying at room temp.

### Cationisation of cotton using Solfix E

The reaction was continued for further 2 hours at 80°C. Then the treated fabrics were neutralized using 2% acetic acid at 40°C/5 min. The treated fabrics were washed using 3 g/l nonionic detergent at 60°C/30 min, followed by washing with water and finally drying at room temp.

### Fastness properties

The dyed samples were tested to washing, fastness properties:

- **Fastness properties:** The color yield of both dyed and mordanted samples was evaluated by light reflectance technique using the Perkin-Elmer, UV/V Spectrophotometer (Model, Lambda 3B). The color strength (K/S value) was assessed using Kubelka-Munk equation.

- **Color-difference formula ΔE CIE (L*, a*, b*):**

  \[
  \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
  \]

  Where:

  - ΔL*: indicates any difference in lightness, (+) if sample is lighter than standard, (−) if darker.
  - Δa*: indicates the relative positions in CIELAB space of the sample and the standard, from which some indication of the nature of the difference can be seen.
  - Δb*: indicates the relative positions in CIELAB space of the sample and the standard, from which some indication of the nature of the difference can be seen.

- **Measurement of the antimicrobial activity using the agar diffusion disc method:** A filter paper sterilized disc saturated with measured quantity of the sample is placed on plate containing solid bacteria medium (nutrient agar broth) or fungal medium (Dox S medium) which has been heavily seeded with the spore suspension of the tested organism. After inoculation, the diameter of the clean zone of inhibition surrounding the sample is taken as a measure of the inhibitory power of the sample against the particular test organism [20-22].

### Testing

**Color measurements of dyed fabrics:** The color yield of both dyed and mordanted samples was evaluated by light reflectance technique using the Perkin-Elmer, UV/V Spectrophotometer (Model, Lambda 3B). The color strength (K/S value) was assessed using Kubelka-Munk equation.
acid and alkaline perspiration, dry and wet rubbing and light fastness according to AATCC standard methods.

**Durability of antibacterial properties:** The durability of the antibacterial effect of the dyed cotton fabric was measured after 5, 10 and 20 washing cycles.

**Results and Discussion**

**Cationisation of cotton fabric using different macromolecules cationising agents**

**Cationisation of cotton fabric using Quat (Table 2b):** Similar to the case of reactive dyeing of cellulosic fibers, the reaction of Quat with cotton fabrics would lead to the formation of ether linkage between Quat and cellulose. However, this desirable reaction will be affected with the side reaction that takes place between Quat and water, thus lowering the efficiency of the treatment process [23,24]. Pad-dry curing technique was used in this work for the pretreatment. The concentration of Quat 50 g/l were used for cotton treatment.

**Cationisation of cotton fabric using Solfix E (Table 2c):** Solfix E is a polyaminochlorohydrin quaternary ammonium polymer with epoxide functionality that can react with cellulose via ether formation in the presence of alkali. Therefore the reactivity of the reagent in aqueous alkaline medium during the pretreatment process is similar to that of reactive dyes during the dyeing process of cellulosic fibers. Especially regarding the hydrolytic effect of water that competes with ether formation.

Based on the well-documented cationisation information in the literature [25,26] the best pretreatment can be obtained by avoiding as much as possible the competing hydrolytic side reaction. To achieve this, the cotton fabric was impregnated with Solfix E in the pretreatment bath at 50°C for 1 h before performing the alkali fixation process.

**The effect of cationic reagent concentration on the nitrogen content of the cationised cotton fabrics**

In a previous report 0.16% nitrogen content was obtained using more than 60 g cationic reagent per 100 g of cotton fabric, however, in this work 0.13% nitrogen content was achieved using less than 40 g of cationic reagent per 100 g of cotton fabric. The effect of cationic reagent concentration on the nitrogen content of the cationised cotton fabrics can be clear that as the nitrogen content of the cotton fabric increases as the concentration of cationic reagent increases. Leveling off at a reagent concentration of 30% owf. This result can be analyzed by the fact that the pretreatment process is a solid-liquid phase reaction, which proceeds by the movement of the cationic molecule from the liquid phase to the solid surface of the fiber by virtue of its ionic interaction with the surface negative charge of cotton fabric. The cationic reagent diffuses within the fabric and becomes covalently fixed to the available primary hydroxyl groups on the fibers, therefore, it is expected that the process is diffusion-controlled and competes with hydrolytic effect of water. Similar behavior has been reported for cationisation using other cationic agents [27] (Scheme 1).

**Effect of using different cationising agents on the color strength**

Table 3 illustrated the results of using different cationising agent and its effects on the color strength and color data. For cotton samples dyed with natural coloring matter extracted from Madder, Logwood, Cutch and Chelidonium majus.

From Table 3, it can be observed that for dyed cotton samples, by using Monochloro-S-Triazine as cationising agent with madder and cutch plants, the highest color strength was achieved. Contrary, using of Solfix E and Quat gave the highest color strength with Logwood and Chelidonium majus plants, respectively.

L*, a* and b* are presented the lightness, red/green ratio and yellow/blue ratio, respectively. Table 3 showed that, L*, a* and b* data are in agreement with color strength results. Values of a* and b* located in the positive region for all dyed samples, indicating that the dyed samples had a yellowish-reddish color. Samples dyed with madder and logwood exhibited more reddish color while the others (Cutch and Chelidonium majus) had more yellowish color.

![Chemical Structure](image_url)

Where:

For CHTAC \( R^1, R^2, R^3 = \text{CH}_3 \)

and for PAQAC \( R^1, R^2=\text{alkyl} \text{ and } R^3=\text{polyamine} \)
From all colorimetric data, the difference in color data may be attributed to the difference in acidity for each plant used. Also, it depends on the concentration of the three cationic agents used in the Pre-treatment.

**Color fastness results**

From Table 4 it can be seen that, fastness properties of fabrics dyed with Madder, Logwood, Cutch and Chelidonium plants were assessed using blue scale. Comparing the fastness properties of the fabrics dyed with different plants, it is found that for all mordants, the dry crocking fastness is good, while the wet one is fair. Also, the acid and alkaline perspiration are good to very good. While, the washing fastness for the Chelidonium plant is the lowest one among the four plants. Finally, the light fastness is very good.

**Antibacterial results**

Table 5 shows the antibacterial properties of dyed fabrics against both *Staphylococcus aureus* (G+) and *Escherichia coli* (G-) bacteria expressed as inhibition zone. It is clear from Table 5 that all samples exhibit antibacterial properties against both types of bacteria. It is clear that the antibacterial properties against *Staphylococcus aureus* (G+) was found to be greater than that of *Escherichia coli* (G-).
repeated washing cycles. To increase the antibacterial activity and increase the stability after cotton dyed with these dyes exhibited stronger antibacterial activity due to the change of surface charge on the cellulose fibers. Cationised increases adsorption of the four natural dyes on the surface of the fibers S-triazine cationic agent, and the cationisation of fabrics strongly Polyaminochlorohydrin quaternary ammonium and Monochloro- using 3-chloro-2-hydroxy propyltrimethyl ammonium chloride, 3. El-Rafie MH, El-Naggar ME, Ramadan MA, Fouda MMG, Al-Deyab SS, et al. References Conclusion can be attributed to the differences in the structure between the two types of bacteria. Table 5 also shows the durability of the antibacterial properties of the treated fabrics with different number of washing cycle (5, 10, and 20 washing cycles). It can be seen from Table 5 that the antibacterial properties are not affected by repeated washing up to 20 washing cycles but in some cases the antibacterial properties increased. It is obvious that the results of antibacterial properties against staph (G+) were found to be greater than that of E. coli (G-) as mentioned above due to the same reason of differences in the structure of bacteria. The antibacterial properties of the treated samples can be attributed to the presence of different types of cationising agents in all cases (Quat, Cationising agent and Solfix). The ability of these cationising agents to form true covalent bonds with cotton fabrics leads to the durability of the antibacterial properties against repeated washing.

Table 5: Antibacterial activity of the dyed cotton with the four natural dyes after 5, 10 and 20 washing cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inhibition zone diameter (mm/1 cm sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Escherichia coli (Gram -ve) bacteria</td>
</tr>
<tr>
<td></td>
<td>5W</td>
</tr>
<tr>
<td>Madder + quat</td>
<td>12</td>
</tr>
<tr>
<td>Madder + cationizing agent</td>
<td>12</td>
</tr>
<tr>
<td>Madder + solifix</td>
<td>13</td>
</tr>
<tr>
<td>Logwood + quat</td>
<td>14</td>
</tr>
<tr>
<td>Logwood + cationizing agent</td>
<td>13</td>
</tr>
<tr>
<td>Logwood + solifix</td>
<td>13</td>
</tr>
<tr>
<td>Cutch + quat</td>
<td>12</td>
</tr>
<tr>
<td>Cutch + cationizing agent</td>
<td>12</td>
</tr>
<tr>
<td>Cutch + solifix</td>
<td>11</td>
</tr>
<tr>
<td>Chelidonium + quat</td>
<td>12</td>
</tr>
<tr>
<td>Chelidonium + cationizing agent</td>
<td>13</td>
</tr>
<tr>
<td>Chelidonium + solifix</td>
<td>12</td>
</tr>
</tbody>
</table>

W: washing cycle