Green Technology for Dyeing of Textile Materials

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**ABSTRACT**
Cotton fibre is one of the most preferred raw materials in apparel industries due to its natural feel and comfort. Fibre reactive dye is the colourant of choice for dyeing cotton fabrics due to its brilliancy, variety of hue and high wet fastness properties. The major challenge in reactive dyeing of cotton is that require large amount of salt for exhaustion, in addition to that extensive water used for removing unfixed dye. The unfixed dye along with added salt increases effluent load on effluent treatment plants and limits the opportunities for recycling treated effluents and cause environmental pollution. This research paper focuses on the modification of cotton fabrics in such a way that the produced fabrics dyed with reactive dyes without the addition of salt thus reduced the effluent load and make the process more sustainable and greener process.

**Keywords**
Reactive dye, Salt, Effluent load, Modified cotton, Greener dyeing process.

**Introduction**
Environmental pollution due to different types of industry is one of the vital problems currently faced and textile industries are the major source that contributes to the environmental pollution. As the textile industries consume large quantities of water, they generate waste water in proportionate order. Moreover the dyes used in the textile industries also pose a serious threat because of high colour, high total dissolved solids (TDS), high chemical oxygen demand (COD), high biological oxygen demand (BOD) and low biodegradability [1, 2]. In general, direct, reactive, vat and sulphur dyes are used for dyeing of cellulosic fibres in which, reactive dye occupies a significant position due to its brilliancy, variety of hues, high wet fastness, convenient usage and high applicability [3-5].

The major challenge in reactive dyeing of cellulosic substrate is that approximately 70-80% of reactive dye is only exhausted in addition to that large quantities of electrolytes are required for exhaustion [6, 7]. The unutilized dye along with added salt used for exhaustion removed as an effluent at the end of the dyeing process [8-10]. This increases the effluent load in terms of total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD) and colour on common effluent treatment plant [6, 11-13]. This high level of effluent load requires advanced tertiary treatment for its removal [14], hence major research attempts are made to improve the exhaustion of reactive dyes and to reduce salt usage in reactive dyeing process.

The efforts on reduction of salt usage can be summarized under the following three categories, namely, the use of low material to liquor ratio (MLR) dyeing so that the quantum of salts used can be reduced [15], low salt dyestuffs from modifications of existing dye [16, 17] and modification of substrate (cotton) to take up dyes uniformly without the use of salt [18, 19, 20].

From the previous attempts, it can be inferred that the modification of the cotton substrate is one of the preferred options for reduction of salt usage in reactive dyeing process [21- 24]. Modification of cotton is carried out by pre-treating the cotton fibers with a reactive cationic agent, so that it could eliminate the amount of salt consumption and subsequent effluent load in reactive dyeing process. In this study quaternary ammonium compound used for modification of cotton garment, this compound will react with cotton under alkaline conditions to form a cationized cotton fiber. This cationized garment was dyed with two different reactive dyes (Green and Navy blue) with darker shades of 10% without the addition of salt. The dyeability and fastness properties of the cationized cotton with different reactive dyes are reported.

**Materials and Methods**

**Materials**
100% cotton garment – scoured, bleached and ready for dyeing garment with 210 g/m2, plain weave woven was used in this study. Commercially available quaternary ammonium compound was used in this study. Hot brand dyes such as Navy (combination) and green (combination) reactive dye was used for dyeing studies and chemicals Glabour’s salt, sodium carbonate, sodium hydroxide were procured from SRL Chemicals Pvt. Ltd., Chennai, India.

**Methods**

**Production of modified cotton**
The quaternary ammonium compound and alkali was applied to the well-prepared cotton garment by exhaust method at 600C for 20 min in the IR dyeing machine. To minimize the hydrolysis of reactant, the alkali was added to the bath just before application. Then the garment rinsed several times with water and finally neutralized with a dilute acetic acid (1 g/l) solution.

**Dyeing of modified cotton and control cotton**
The modified cotton garments were dyed with 10% shade of reactive dye (Navy and Green). The garment was introduced into a bath containing the dye at the room temperature and the temperature was gradually raised to 40°C.
The dyeing was continued till the end of the primary exhaustion without the addition of salt according to the procedure given by the dye manufacturer. Then, the required amount of alkali was added and dyeing was continued till the end of the fixation time. A control sample was also dyed as per the procedure given by the manufacturer with the addition of salt for 10% shade which was used as a control for this study. The material to liquor ratio (MLR) for dyeing was kept at 1:50. Once dyeing was completed, the dye bath was drained and a fresh batch of water was introduced. The garment was hot rinsed at 45°C and soaping process was carried at a temperature range of (90°C) for 10 minutes as per the recommendations of the manufacturer. The liquor was drained, refilled with water and a cold wash with running tap water for 10 minutes and finally all samples were air dried.

**Colour strength evaluation**

The colour strength of the dyed garment was measured using UV-visible spectrophotometer for the control and modified cotton dyed samples. The colour strength was expressed in terms of K/S values. Kubelka-Munk equation (K/S) defines a relationship between spectral reflectance of the sample and its absorption (K) and scattering (S) characteristics. The colour strength (K/S) value was calculated using the formula given below using a UV visible spectrophotometer.

\[
K/S = (1-R)/2R
\]  

Where, K is the coefficient of absorption, S is the coefficient of scattering; and R is the reflectance value of the garment at \( \lambda_{\text{max}} \). The relative colour strength percentage between modified cotton and control dyed samples was also obtained using the following relationships.

Relative colour strength (RCS %) = \( \frac{(K/S \text{ value of modified cotton dyed sample})-(K/S \text{ value of Control}) \times 100}{(K/S \text{ value of Control})} \)  

Where, 

\[
L^* = 116 \left( \frac{Y/Y_0} {Y_0} \right)^{1/3} - 16 \]  
\[
a^* = 500 \left( \frac{X/X_0} {X_0} \right)^{1/3} - (Y/Y_0)^{1/3} \]  
\[
b^* = 200 \left( \frac{Y/Y_0} {Y_0} \right)^{1/3} - (Z/Z_0)^{1/3} \]  
\[
Chroma (C^*) = \sqrt{(a^*)^2 + (b^*)^2} \]  

\[
\text{Hue} (h^*) = \tan^{-1} (b^*/a^*) \]  

L - Lighter/darker; \( a^* \) - redder/greener; and \( b^* \) - yellower/bluer. The hue and chroma values were calculated using L, a, b values.

**Fastness testing**

The selected garment samples (control, modified cotton garment) were tested for colour fastness to washing according to ISO 687 - 1979. Fastness to rubbing and perspiration were tested according to ISO 766 - 1988 and ISO 971 - 1956, respectively and the colour change was rated according to the appropriate gray scale. Colour fastness to light was tested according to ISO 2454 – 1985 and the degree of fading was assessed by SDC blue wool scales.

**Results and Discussion**

**Chemistry of modified cotton**

The reaction of cationic agent with cotton garment was done in situ by the reaction of quaternary ammonium compound with alkali at 600°C for 20 min during which the quaternary compound reacts with cotton, as a result cotton will have cationic reactive sites. These cationic sites will strongly attract anionic reactive dyes without the addition of electrolyte that is normally needed to drive the dyes from the water onto the cotton fiber.

**Dyeing results**

Reactive dyes with various reactive dyes were examined to assess their suitability for use on the modified cotton.

The results showed that all of the dyes employed gave an excellent exhaustion with 10% o.w.f. and most of them showed a high fixation with good levelness. Also, the reactive dyes were applied to control cotton, according to the manufacturer recommendations. The results for three different dyes are listed in Table 1.

It can be seen that the colour strength values for the modified cotton with the above two dyes is two to five times higher than those on the control cotton without the addition of salt. The colour coordinates values such as \( (L^*, a^*, b^*, L^o, C^o) \) denotes that the modified cotton dyed with navy become deep in darker due to the decreased \( L^o \) and \( C^o \) vale. Similarly the green dyed modified cotton is also looking darker in shade due to decreased colour coordinates values. Modified cotton fabric dyed without the addition of salt itself gave extremely higher colour strength than the control cotton fabric and the effluent is also contains a less TDS content due to the absence of salt, however, a detailed study on effluent characteristic was carried out as a separate research work in further, thus modified cotton fabric is a good starting material for environmentally friendly reactive dyeing process.

**Colour strength evaluation from reflectance curve**

The reflectance curve for the sample is given in the Figure 1, from the Figure it can be seen that for 10% shade the reflectance curve of modified cotton garment dyed with 2 different dyes follows the same path as like control sample and it shows that modified cotton garment matches closely to the control samples in terms of colour parameters. The K/S values and relative colour strength of the samples are tabulated in Table 1. From the Table 1 it can be seen that all the modified cotton garment gives relative colour strength of 200% to 500% compared to the control sample. From the reflectance curve it shows that modified cotton dyed garment is similar to that of control sample in terms of tone. Figure 2 shows the photographic images of the control and modified cotton dyed fabrics and it clearly shows that the modified cotton dyed fabrics were very darker in depth compared to that of the control dyed fabrics.

### Table 1. Colour strength (K/S) values for control and modified cotton garments without salt.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Samples</th>
<th>K/S</th>
<th>RCS (%)</th>
<th>( L^* )</th>
<th>( a^* )</th>
<th>( b^* )</th>
<th>( h^* )</th>
<th>( C^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Navy</td>
<td>Control</td>
<td>10.31</td>
<td>100</td>
<td>28.87</td>
<td>3.52</td>
<td>-14.06</td>
<td>76</td>
<td>14.49</td>
</tr>
<tr>
<td></td>
<td>Modified</td>
<td>24.26</td>
<td>235</td>
<td>16.33</td>
<td>3.53</td>
<td>-6.57</td>
<td>61.74</td>
<td>7.46</td>
</tr>
<tr>
<td>Green</td>
<td>Control</td>
<td>5.058</td>
<td>100</td>
<td>44.30</td>
<td>-17.25</td>
<td>11.42</td>
<td>33.42</td>
<td>20.69</td>
</tr>
<tr>
<td></td>
<td>Modified</td>
<td>25.46</td>
<td>503</td>
<td>19.44</td>
<td>-8.491</td>
<td>3.91</td>
<td>24.7</td>
<td>9.35</td>
</tr>
</tbody>
</table>

These cationic dyestuffs can be used to dye the modified cotton fabric which has shown higher colour strength than the control cotton fabric and the effluent is also contains a less TDS content due to the absence of salt, however, a detailed study on effluent characteristic was carried out as a separate research work in further, thus modified cotton fabric is a good starting material for environmentally friendly reactive dyeing process.
Colour fastness studies

The samples were tested for colour fastness to washing and perspiration using the Society of Dyers and Colourists (SDC) standard multifibre garment. The standard grey scales for assessing change in colour and staining properties were used to obtain ratings. Table 2 outlines the results of the colour fastness properties.

Table 2. Colour fastness results for control and modified cotton dyed sample.

<table>
<thead>
<tr>
<th>Colour fastness to</th>
<th>Colour change &amp; Staining</th>
<th>Control</th>
<th>Modified cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing</td>
<td>4-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perspiration (Acid)</td>
<td>4-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perspiration (Alkali)</td>
<td>4-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rubbing Dry</td>
<td>4-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>4-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The grey scales are used to rate any change in colour or any staining that occurs on samples that have been tested for their colour fastness properties to washing, perspiration, water and rubbing. The grey scales for colour change and staining is a scale of 1 to 5; 5 being the best with no colour change or staining occurring and 1 being the worst where there is a large colour change from the original sample or staining from the tested sample to the standard garment. A blue scale is used to rate samples that have been tested for colour fastness to light. The blue scale is exposed with the tested samples, the rating scale from 1 to 8; 8 being the best with no change and 1 being the worst with significant change.

Table 2 shows that the colour fastness results for the control and modified cotton sample indicate that it has relatively good colour fastness to washing and both the acid and alkali perspiration tests and received a grey scale rating of 4-5 for all the samples. For the colour fastness to rubbing test the control sample received a rating of 4-5 and for the fastness to light a blue scale rating of 7 was achieved.

Conclusions

The cotton garment treated with a quaternary ammonium compound provides cationic sites which can be dyed with reactive dyes without electrolytes (salt) to give excellent results. Reactive dyes can be exhausted almost entirely onto the modified cotton fabric, thus it gave a minimum of twice the colour strength as that of the control fabric dyed by the conventional method. The tone of the garment was not altered in the modified cotton dyed garments and the colour fastness of this dyed garment is almost equal to that of the control cotton. Thus the use of modified cotton in reactive dyeing processing has twofold advantage. Initially, consume 100% dyes thus eliminating coloured effluent discharge and finally eliminate the salt consumption for exhaustion of reactive dyes on cotton garment to reduce the pollution load, hence modified cotton is a good raw material for eco-friendly dyeing process.

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References


