CHAPTER V

STUDY ON THE USE OF TRISODIUM CITRATE AS BIO-SALT IN DYEING OF COTTON
CHAPTER V

STUDY ON THE USE OF TRISODIUM CITRATE AS BIO-SALT IN DYEING OF COTTON

5.1. Introduction

Ecofriendly textile wet processing are gradually gaining importance in recent times due to environmental issues throughout the world. Consumers in the developed countries are looking for biodegradable and ecofriendly textiles [1-3]. In dyeing of textiles, ecological restrictions are strictly followed from raw material selection, processing and water management to the final product. This has become more serious since the German ban came into effect [4]. The main challenge before the textile industry today is to modify the production at a competitive price by using safe dyes and chemicals as well as by reducing treatment cost.

Cotton acquires negative charge in aqueous medium and thus repels negatively charged dye anion during dyeing. Using large quantity of salt in dye bath, particularly for reactive dyes, offsets such repulsion between fibre and dye. Low dye bath exhaustion leads to low dye fixation of reactive dyes on cotton. Thus, the use of high salt concentration and low reactive dye fixation leads to environmental problems related to highly colored effluent with high total...
dissolved solids content. These problems can be reduced by improving the dye substantivity of cotton in the absence of salt or with low salt addition [5].

Certain dyes belonging to azoic, basic, direct, disperse, acid and oxidation colors are termed as red listed dyes due to German ban [6]. Dyes from the remaining classes, viz. reactive, vat, sulfur and natural dyes have not been banned. Although these dyes are unaffected or safe dyes, the practical dyeing with them are not free from the environmental problems. Dyeing with vat, sulfur, reactive and natural dyes requires large quantities of salts to achieve good exhaustion, which increase the total dissolved solids (TDS) in effluents [7]. Natural dyes are normally ecofriendly, but the metallic mordants used for improving fastness and better fixation on textiles is not ecofriendly [8].

5.1.1. Reactive dyeing

Burlington Industry has discovered the reactive dyes containing phosphonic acid and carboxylic acid reactive group for dyeing without salt. The main disadvantage of these dyes is the tendering of cotton [9]. Use of Sumifix Supra dyes overcomes the drawbacks of low degree of exhaustion, fixation, poor levelness, poor reproducibility and low wet fastness [10]. The dyeing effluent containing unabsorbed dye, surfactants, auxiliaries and other chemicals may increase the pollution load. The removal of dye [11] and surfactants [12] from effluent has been reported.
The Japanese manufacturer [13,14] sells some of the cationic cotton in the International market. The dyeing process for cotton, particularly with reactive dyes with the objective of minimizing the effluent problems has been examined [15]. The model cationic reactive dyes used in this study was prepared by incorporation of a chlorotriazine reactive group into the basic dye chromophore containing localized cationic charge. The application of model cationic reactive dye to cotton was carried out by a conventional dyeing method without the addition of salt. The dyeing properties, particularly light and wash fastnesses have been discussed well [16].

5.2. Bio-salt

Citrate salts such as trisodium citrate, tripotassium citrate and triammonium citrate are finding major importance in food and beverage industries. They are used as an emulsifier, stabilizer, acidity and flavor modifier. These compounds are also used in medical, cosmetics and toiletries, in industrial applications and household cleaners [17].

Sodium sulfate (SS) and sodium chloride (SC) salts are presently employed as exhausting agents in dyeing of cotton. The dye effluent contains higher TDS values. In order to reduce the TDS content and to develop an ecofriendly alternative, trisodium citrate (TSC) salt was selected as model
compound. This investigation was aimed to explore the possibility of using trisodium citrate salt as an exhausting agent in dyeing of cotton with reactive, direct and solubilized vat dyes. Exhaustion behavior of TSC electrolyte was compared with that of sodium sulfate (SS) and sodium chloride (SC). TDS values for spent dye liquors and fastness values for fabrics were studied and presented.

5.3. Experimental details

Bleached cotton woven fabric (ends per inch = 60, picks per inch = 52, weight = 67 gm / yard², count = 10s) was used for this study. In dyeing experiments, conventional sodium chloride and bio-salt trisodium citrate were used as exhausting agents. Sodium carbonate and non-ionic wetting agent (sandozin NIE) were used as dyeing auxiliaries. Reactive dye (Procion Red HE3B), direct dye (Solar Turquoise Blue GLL) and solubilized vat dye (Arlindone Golden Yellow IGK) were used.

Cotton fabric was subjected to three different dyeing (reactive, direct and solubilized vat) experiments separately.

5.3.1. Reactive dyeing

Bleached cotton fabric was first wetted with water. The wetted fabric was then entered into the dye bath containing required amount of water at 40°C. After a gap of 5 min, calculated amount of dye solution was added. Again after
a gap of 5 min, required amount of exhausting agent was added and heated. Then, alkali was added and the temperature was maintained. Then, the dyed fabric was taken out, washed, neutralized, squeezed and dried.

5.3.2. Direct dyeing

Bleached cotton fabric was first wetted with water. The dye bath was set with dye solution and water at a MLR 1:20. The wetted fabric was then entered into the dye bath. After the addition of necessary additives, the temperature was maintained for a selective time. Then the dyed sample was washed with water and dried.

5.3.3. Solubilized vat dyeing

Bleached cotton fabric was first wetted with water. The wetted fabric was then entered into the dye bath containing the additives. The dyeing was done. Then, a developing treatment with a solution containing 2 g/l hydrogen sulfate and 10 g/l sodium nitrite was followed. After this, the fabric was washed with water and dried.

5.3.4. Effect of dyeing parameters

In order to obtain optimum conditions in cotton dyeing with reactive, direct and solubilized vat dyes, the following dyeing parameters were studied.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range examined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye concentration (%)</td>
<td>1, 2, 3, 4</td>
</tr>
<tr>
<td>Exhausting agent concentration (%)</td>
<td>2, 4, 6, 8</td>
</tr>
<tr>
<td>Time (min)</td>
<td>30, 45, 60, 75</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40, 60, 80, 100</td>
</tr>
</tbody>
</table>

Bleached cotton fabrics were again dyed under the optimum dyeing conditions obtained for 3 different methods. The dyed fabric samples were then washed, soaped and dried separately.

The dye bath liquor was tested for total dissolved solids (TDS) content before and after dyeing process by a Merck make TDS meter. The dye uptake of dyed fabric samples were obtained by measuring the difference in absorbance of the dye bath concentration before and after dyeing using Jasco-V-530-UV-Visible spectrophotometer and dye bath exhaustion was calculated.

5.4. Results and discussion

5.4.1. Effect of dye concentration

As the dye concentration increased from 1 to 4%, the dye uptake increased gradually for sodium chloride exhaustion for all three dyeing methods studied (Table 5.1). In the case of trisodium citrate exhaustion, the dye uptake reached a maximum for 2% dye concentration in direct dyeing and 3% dye concentration for both reactive and solubilized vat dyeing methods. During
dyeing, the other variables were kept constant (electrolyte 6 / 4 / 6%, time 60 / 60 / 60 min, temperature 80 / 100 / 40°C in reactive, direct and solubilised vat dyeing, respectively. Dye uptake obtained are between 45 and 65% using sodium chloride and between 65 and 90% using trisodium citrate. Sodium sulfate produced a dye uptake value, which lies in the range obtained for sodium chloride and trisodium citrate. Dye uptake noticed are more with trisodium citrate exhaustion than with sodium chloride exhaustion in all three dyeing methods. About 20% dye uptake improvement is noticed with trisodium citrate when compared to sodium chloride (Figure 5.1).

As the dye concentration increased, the dye uptake increased for all the three dyeing methods with trisodium citrate and they are ranked in the order reactive > solubilized vat > direct. This may be due to the formation of strong covalent bonds in reactive dyeing and weak hydrogen bonds in direct dyeing.

5.4.2. Effect of exhausting agent concentration

The concentration of exhausting agent was increased from 2 to 8% keeping other parameters constant. In reactive dyeing, 3% dye concentration was used at 80°C for 60 min. In direct dyeing, 2% dye concentration was used at 100°C for 60 min. And in solubilized vat dyeing, 3% dye concentration was used at 40°C for 60 min. The dye uptake values increased in all three dyeing methods with sodium chloride exhaustion, but almost no change in dye uptake
is noticed in direct and solubilized vat dyeing methods with trisodium citrate exhausting agent.

A little improvement in dye uptake is noticed for reactive dyeing with trisodium citrate up to 6% concentration. In all three dyeing methods, at lower concentration of exhausting agent (2%), trisodium citrate produced better dye uptake than sodium chloride and sodium sulfate did.

It is evident from the results that lower concentration of exhausting agent (2%) using trisodium citrate produced better dye uptake. 2% Trisodium citrate produced better dye uptake than 8% sodium chloride did in all three dyeing methods (Figure 5.2). This is very important in the present day goal of lowering salt concentration in ecofriendly dyeing methods. The absorption of these dyes by the fabric could be ranked as reactive > solubilized vat > direct.

5.4.3. Effect of dyeing time

At other fixed variables (dye 3%, electrolyte 6%, temperature 80°C in reactive dyeing / dye 2%, electrolyte 2%, temperature 100°C in direct dyeing / dye 3%, electrolyte 2%, temperature 40°C in solubilized vat dyeing), dyeing experiments were performed. As the dyeing time increased from 30 to 75 minutes, the dye uptake also increased gradually up to 60 minutes and almost remains constant for further increase in dyeing time in all dyeing methods studied. Trisodium citrate exhaustion produced better dye uptake than sodium...
chloride and sodium sulphate exhaustion in all three dyeing methods (Figure 5.3).

5.4.4. Effect of temperature

The effect of dyeing temperature was studied. As the temperature of dyeing increased, the dye uptake increased for reactive and direct dyeing methods with both sodium chloride and trisodium citrate. In solubilized vat dyeing, the dye uptake decreased with increase in dyeing temperature from 40 to 100°C for both sodium chloride and trisodium citrate exhaustion. Trisodium citrate exhaustion produced better dye uptake than sodium chloride and sodium sulfate exhaustion in all three dyeing methods (Figure 5.4).

The optimum conditions obtained using sodium chloride, sodium sulfate and trisodium citrate exhaustion in three different dyeing methods are compared and given in Table 5.2. It is clear from the table that trisodium citrate is well suitable for the replacement of sodium chloride / sodium sulfate in different dyeing methods in order to achieve the goal of salt reduction.

When a cellulosic fibre is immersed in dye liquor, it acquires a negative electrical charge. The negatively charged fibre surface repels the negatively charged dye ions present in the dye bath. When salts (cations) are added to the dye bath, they try to neutralize or reduce the negative charge of the fibre, thereby facilitating the dye anions for the formation of bonds between the dye
and the fibre. If a dye contains more sulphonlic acid or chloride groups, its ions will accordingly acquire more negative charges and will be repelled by the fibre with greater force. Therefore, the effectiveness of a salt in promoting exhaustion varies directly with the number of sulphonlic acid or chloride groups in the dye molecules.

In this investigation, the dye uptake values obtained in 3 dyeing methods using trisodium citrate as an exhausting agent is higher than sodium chloride and sodium sulfate did. The trisodium citrate (3 Na\(^+\)) is higher cationic in nature than sodium sulfate (2 Na\(^+\)) and sodium chloride (Na\(^+\)). So, the dye in the presence of trisodium citrate is more attracted by the cotton fabric than with sodium chloride. Hence, better exhaustion is noticed with trisodium citrate than sodium chloride.

Presently, the cost of trisodium citrate is about 3 times higher than sodium chloride costs. But the amount of sodium chloride used in this dyeing process is 4 parts when compared to 1 part of trisodium citrate for producing the same depth of shade. The 1% dye concentration using trisodium citrate exhausting agent produced relatively similar result in dye uptake when compared using 4% dye concentration with sodium chloride.
5.4.5. Fastness properties

Reactive and solubilized vat dyed samples produced better fastness properties than direct dyed samples did. Dyed samples using trisodium citrate as an exhausting agent produced better wash, light and rub fastness properties than other exhausting agents did (Figure 5.5). Trisodium citrate exhausting agent treated samples produced good fastness properties than sodium chloride (Table 5.3).

5.4.6. Total Dissolved Solid (TDS)

The spent dye bath liquors were analyzed for TDS content. The effluent produced in dyeing of cotton using sodium chloride and sodium sulfate showed higher TDS values, which may be due to the excess amount of salt used for exhaustion. Higher TDS and lower dye uptake values were noticed for sodium chloride exhausting agent, but, higher dye uptake and lower TDS values were noticed for trisodium citrate exhausting agent.
5.5. Conclusion

The inorganic conventional exhausting agents (sodium chloride and sodium sulfate) are widely used in textile processing. It poses environmental problems. It can be successfully replaced by ecofriendly bio-salt (trisodium citrate) as an exhausting agent. Dyeing using bio-salt (trisodium citrate) produced higher dye uptake and lower TDS values than using sodium chloride and sodium sulfate. These are very important in the present day environmental problems.

Reactive and solubilized vat dyed samples produced better dye uptake and fastness properties than direct dyed fabrics did. In general, all dyeing experiments using trisodium citrate as an exhausting agent produced higher dye uptake and lower TDS values. The efficiency of trisodium citrate in dyeing is found to be better than sodium chloride and sodium sulfate.
References

2. Bot and V. Vreeswijk; Mellandi Textilber, 20 (1939) 115.
Table 5.1: Effect of variables in dyeing

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Dye uptake (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reactive</td>
<td>Direct</td>
<td>Solubilized vat</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SC</td>
<td>SS</td>
<td>TSC</td>
<td>SC</td>
</tr>
<tr>
<td>Dye conc. (%)</td>
<td></td>
<td>1</td>
<td>62.5</td>
<td>68.1</td>
<td>82.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>63.3</td>
<td>69.8</td>
<td>84.3</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>65.6</td>
<td>77.3</td>
<td>89.0</td>
<td>54.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>70.7</td>
<td>79.6</td>
<td>89.1</td>
<td>58.2</td>
</tr>
<tr>
<td>Exhausting agent conc. (%)</td>
<td>2</td>
<td>60.2</td>
<td>69.5</td>
<td>82.2</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>68.0</td>
<td>73.2</td>
<td>84.8</td>
<td>58.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>70.1</td>
<td>78.6</td>
<td>89.3</td>
<td>59.0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>74.3</td>
<td>80.4</td>
<td>89.4</td>
<td>64.6</td>
</tr>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>58.2</td>
<td>62.3</td>
<td>75.1</td>
<td>43.6</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>60.5</td>
<td>64.5</td>
<td>76.4</td>
<td>49.4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>66.3</td>
<td>67.5</td>
<td>84.8</td>
<td>52.2</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>65.8</td>
<td>70.3</td>
<td>84.8</td>
<td>53.7</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>40</td>
<td>59.4</td>
<td>61.2</td>
<td>78.2</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>64.3</td>
<td>65.4</td>
<td>84.3</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>66.8</td>
<td>69.7</td>
<td>86.6</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>65.4</td>
<td>71.0</td>
<td>88.7</td>
<td>55.8</td>
</tr>
</tbody>
</table>

SC - Sodium chloride  
SS - Sodium sulfate  
TSC - Trisodium citrate
Table 5.2: Optimized values for exhausting agents in 3 dyeing methods

<table>
<thead>
<tr>
<th>Dyeing method</th>
<th>Variable Studied</th>
<th>Range examined</th>
<th>SC</th>
<th>SS</th>
<th>TSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive</td>
<td>Dye concentration (%)</td>
<td>1,2,3,4</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Electrolyte concentration (%)</td>
<td>2,4,6,8</td>
<td>8</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Time (min)</td>
<td>30,45,60,75</td>
<td>75</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>40,60,80,100</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Direct</td>
<td>Dye concentration (%)</td>
<td>1,2,3,4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Electrolyte concentration (%)</td>
<td>2,4,6,8</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Time (min)</td>
<td>30,45,60,75</td>
<td>75</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>40,60,80,100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Solubilized Vat</td>
<td>Dye concentration (%)</td>
<td>1,2,3,4</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Electrolyte concentration (%)</td>
<td>2,4,6,8</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Time (min)</td>
<td>30,45,60,75</td>
<td>60</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>40,60,80,100</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.3: Dye uptake and TDS values in different dyeing methods

<table>
<thead>
<tr>
<th>Dyeing method</th>
<th>SC</th>
<th>SS</th>
<th>TSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dye uptake</td>
<td>TDS</td>
<td>Dye uptake</td>
</tr>
<tr>
<td>Reactive</td>
<td>66.7</td>
<td>34800</td>
<td>74.34</td>
</tr>
<tr>
<td>Direct</td>
<td>58.2</td>
<td>3800</td>
<td>62.10</td>
</tr>
<tr>
<td>Solubilized Vat</td>
<td>62.7</td>
<td>6900</td>
<td>68.40</td>
</tr>
</tbody>
</table>
Figure 5.1: Effect of dye concentration in reactive (R), direct (D) and solubilized vat (SV) dyeing methods with exhausting agents (SC & TSC)

Figure 5.2: Effect of exhausting concentration in reactive (R), direct (D) and solubilized vat (SV) with exhausting agents (SC & TSC)
Figure 5.3: Effect of dyeing time in reactive (R), direct (D) and solubilized vat (SV) with exhausting agents (SC and TSC)

Figure 5.4: Effect of dyeing temperature in reactive (R), direct (D) and solubilized vat (SV) with exhausting agents (SC and TSC)
Figure 5.5: Effect of fastness in reactive (R), direct (D) and Solubilized vat (SV) with exhausting agents of SC and TSC.