Bioscouring of cellulosic textiles


1. Introduction

Cotton fibres consist mainly of high molecular weight, long chain cellulosic molecules that are polymerised from β-d-glucose monomers. Being organically produced, the cellulose component is associated with small quantities of proteins, oily products, pectins, colouring matter and some mineral salts.

These non-cellulosic components are located in the outermost cuticle layer (that is 0.5-0.1 µm thick) and the primary wall of the cotton fibres. The non-cellulosic constituents are considered as impurities of cotton in the manufacturing processes and are therefore removed by treatment with the hot caustic soda solution before dyeing, printing and finishing of the material. Depending upon variety of cotton, quantity of these impurities ranges between 6% to 9%. Proportion of the constituents of this non-cellulosic matter in the whole fibre and the cuticle may be seen in the following Table 1.

Of all the non-cellulosic impurities, proteins form the largest group and exist mainly in lumen although part of it is present in the primary wall. The pectin is present as a polymer of D galacturonic acid residues forming block copolymers. It is covalently linked with cellulose and is also attached to the calcium ions by Coulombic interactions.

The waxes are present in the primary wall and are responsible for the hydrophobic nature of cotton fibres. The waxes consist of various hydrocarbons, fatty alcohols and fatty acids and their esters. The ash represents mostly as phosphates and oxides of potassium, sodium, calcium, magnesium and iron cations and is highly alkaline.

2. Use of enzymes in textile wet processing

The non-cellulosic constituents of cotton fibres are commonly removed by scouring with a caustic soda solution at temperatures near or above the boiling point of the scouring liquor. The alkaline scouring treatment emulsifies the waxes and breaks down pectin and proteins into water soluble or water emulsifiable products that are later washed off the cotton materials.

The treatment is very effective for a thorough removal of all the impurities except the colouring matter but it is energy, chemical and water intensive and above all the effluent is ecologically undesirable due to its high BOD, COD and alkalinity.

These drawbacks of the process led to consideration for alternatives and bioscouring with suitable enzymes appears to be most promising in this respect. Use of enzymes in the textile wet-treatments is already established for a number of processes. The enzyme amylase has been used for centuries to remove the starch sizes from the cotton fabrics.

Cellulase enzyme is used to remove loose fibres from the surface of the cotton fabrics to impart a smooth and brighter finish, commonly termed as ‘biopolishing’. Production of ‘aged’ denim jeans with cellulase with or without ‘stone washing’ is increasingly practiced as about a billion pairs of jeans, that are produced annually using this processing technique. Removal of residual hydrogen peroxide after bleaching is now done by the enzyme oxidase and has greatly replaced use of sodium bisulphite. The increasing use of enzymes in the industry has been greatly facilitated as effluent wastes of these processes is relatively eco-friendly and their treatment before disposal is cost effective. A brief review of the nature of enzymes is given below.

3. Nature and function of enzymes

Enzymes are high molecular weight proteins that are produced by living organisms. These are composed of about 200 to 250 amino acids that catalyse (i.e. lower the activation energy) of many organic reactions without being consumed in the process. Enzymes activity can, however, be reduced or completely destroyed (denatured) by high temperatures, extremes of pH and high concentration of electrolytes that destroy their 3-dimensional structures. Heavy metal ions, oxidizing and reducing agents also deactivate the enzymes. Certain enzymes require bivalent metal cations as activators to stabilise the structure of the enzyme-substrate complex.

Enzymes or biocatalysts are very specific in their reactions and there is a different enzyme for each part of a series of reactions like those occurring in the vegetable and animal life processes. Their function is often compared with the specificity of a lock and key but actually their functioning is much more complex than what this simple analogy might suggest. Enzymes themselves are biodegradable and are converted into harmless substances in the effluent.

4. Bioscouring with enzymes

A great deal of research work has been carried out during the last 10 years to study the effect of different enzymes for removing the non-cellulosic constituents from cotton, linen and lignocellulosic (used in the paper industry) and their effects on the properties of the substrates. Some of relevant studies are briefly reviewed here.

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition of whole fibre (percentage)</th>
<th>Percentage in cuticle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>88-96</td>
<td>--</td>
</tr>
<tr>
<td>Protein</td>
<td>1.1-1.9</td>
<td>36.4</td>
</tr>
<tr>
<td>Pectin</td>
<td>0.7-1.2</td>
<td>19.6</td>
</tr>
<tr>
<td>Waxes</td>
<td>0.4-1.0</td>
<td>17.4</td>
</tr>
<tr>
<td>Ash</td>
<td>0.7-1.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Seed-Coat Fragments</td>
<td>0.5-1.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 1
4.1. Pectinase on cellulose

Pectin appears to act as a matrix or cement that stabilises the cuticle and primary wall of the fibres. Digestion of the pectin by the pectinase enzyme loosens the matrix and then the unbound waxes and proteins become easily emulsifiable in a hot water scouring. The treatment improves absorbency and also whiteness of the material.\textsuperscript{5,6,7} During the usual treatment time of about 30 minutes or so, about 30\% of the pectin is digested but that is enough to destabilise the structure and release of the non-cellulosic products for emulsification. Sorption and dye uptake of the pectinase treated fabrics have been compared with the conventional alkali scoured ones and the studies indicate a slightly higher sorption of water by the former but there is no difference in the values of K/S.\textsuperscript{8}

4.2. Protease

Common protease enzymes remove about 50\% of the protein, but do not significantly improve the wettability of the fibres. This indicates that protein is removed from the lumen and not from the primary wall.\textsuperscript{9} Some workers\textsuperscript{10} however, have found that certain types of protease improve water absorption and also lighten colour of the fibres.

4.3. Lipases

Lipase enzyme hydrolyses the ester group of the waxes to form glycerol and fatty acids. However, this treatment does not alter water sorption or wettability of the cotton material. It has no effect on the strength of the fibre also.

4.4. Cellulase

Cellulase improves water sorption considerably but there is noticeable loss in weight and also the tenacity of the material is reduced.\textsuperscript{9}

4.5. Combined enzymes

Combination of enzymes has some synergetic effect and the most commonly used combination of cellulase and pectinase improves wetting of the cotton fibres. Cellulase breaks down the cuticle and the primary wall structure and thus promotes penetration of pectinase for more complete breakdown of the gummy and binding pectin. This combination also helps in lowering the concentration of the pectinase but there is a relatively greater loss in weight.\textsuperscript{9,11}

4.6. Effect of sequestering agents

There was some controversy regarding the effect of sequestering agents on the efficacy of the enzymes but Losonczi’s work\textsuperscript{12} has clearly shown that addition of EDTA accelerates hydrolysis of Pectin.

EDTA removes calcium ions that form cross-bridges in pectin and thus makes it more accessible for action of the enzyme. However, if EDTA is used as a pre-treatment, efficiency of the pectinase and xylase enzymes is reduced, due probably to the precipitation of pectin into a more compact and so a less accessible structure. Certain enzymes having an associated metal atom are adversely affected by EDTA because it tends to remove the metal from the enzyme-metal complex and thus disrupts its normal functioning.

5. Aims of the study

The main purpose of the work is to study the effect of the bioscouring process on the medium staple length (24-26 mm) Pakistani cotton on its colour removal, water absorbency and tensile strength and to compare these with the conventional Solomatic scoured and bleached cotton.

The experimental work was carried out on hanks of 20 single cotton yarn weighing 2 grams each. Yarn was selected in preference to the cotton fabric because it does not carry the starch size that is difficult to remove completely even after prolonged desizing with the amylase enzyme.

The enzyme used for bioscouring was pectinase that was supplied by Novozymes, and is marketed under the trade name ‘Scourzyme L’. The grey cotton yarn hanks were bioscourged with 0.5\% pectinase enzyme and 0.5 ml/I of a non-ionic wetting agent at 55°C for 20 minutes.

Temperature of the bath was then raised to 85°C and then 0.5 g/I of EDTA (a sequestering agent) and 0.5 g/I of an emulsifier were added and the treatment continued for another 10 minutes. The bath was then dropped and the hanks washed with hot and cold water. The bioscourged hanks were then dried in an oven at 110°C.

To compare the results of whiteness achieved by bioscouring, the grey yarn hanks were solomatically bleached as per the following recipe.

<table>
<thead>
<tr>
<th>Type of Treatment</th>
<th>Absorbency (Height of dye liquor)</th>
<th>Whiteness Illuminant F11 10 deg</th>
<th>Tenacity (Newtons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey</td>
<td>0.25 cm</td>
<td>13.35</td>
<td>64.17</td>
</tr>
<tr>
<td>Bioscoured</td>
<td>8.5 cm</td>
<td>22.30</td>
<td>64.60</td>
</tr>
<tr>
<td>Full Solomatic Bleached (non-bioscoured)</td>
<td>7.0 cm</td>
<td>76.18</td>
<td>55.70</td>
</tr>
<tr>
<td>Bioscoured and Full Bleached</td>
<td>8.5 cm</td>
<td>76.99</td>
<td>--</td>
</tr>
<tr>
<td>Bioscoured and Bleached (25% less H$_2$O$_2$)</td>
<td>7.0 cm</td>
<td>76.01</td>
<td>--</td>
</tr>
<tr>
<td>Bioscoured and Bleached (50% less H$_2$O$_2$)</td>
<td>6.6 cm</td>
<td>77.69</td>
<td>--</td>
</tr>
<tr>
<td>Bioscoured and Bleached (75% less H$_2$O$_2$)</td>
<td>8.0 cm</td>
<td>74.69</td>
<td>70.75</td>
</tr>
</tbody>
</table>

The bioscourged hanks were also bleached under the above conditions but with increasingly lower concentrations of hydrogen peroxide as detailed in the Table-2.
After the hydrogen peroxide treatment, the yarn hanks were washed with hot and cold water, treated with 2 g/l sodium bisulphite solution and then washed again with hot and cold water. The conventionally bleached hanks were compared for loss in weight, absorbency, whiteness and tenacity with the bioscoursed as well as with the bioscourced and then bleached with hydrogen peroxide of varying concentrations.

The absorbency tests were carried out as per ISO 9073-6, using 5g/l of a Direct dye ‘Solar Turquoise Blue FBL.

Whiteness of the samples was compared on the Datacolor spectrophotometer.

Tenacity of the hanks was determined under the standard conditions of temperature and humidity on Testometric 220D yarn strength tester. An average of 6 hanks was taken as the final value.

6. Results and discussion

6.1. Loss in weight after scouring and bleaching

Loss in weight of the Solomatic bleached hanks, as per the above recipe (Section 5) was 4.4% while that of bioscourced and bleached with half the quantity of the hydrogen peroxide was 2.3%, showing a net gain in weight for comparable whiteness of the material of 2.1%. The loss in weight after bioscouring without the peroxide bleaching was only 1.23%.

6.2 Absorbency, tenacity and whiteness: Tests for these parameters were carried out on the yarn hanks in the grey, bioscourced, grey full bleached and the bioscourced and full bleached as per the recipe given in section 5.

Additional samples of the bioscourced yarn were bleached with the decreasing quantities of hydrogen peroxide as (a) 25%, (b) 50% and (c) 75% less quantity of that of the standard recipe for full bleach. Results of these studies are tabulated below.

7. Conclusions

7.1. Absorbency

There is a remarkable improvement in the absorbency of the bioscourced yarn that is even better than that obtained by the conventional Solomatic bleached grey yarn. Results of the bioscourced and then bleached with varying concentrations of hydrogen peroxide show a general trend of high absorbency equal to that of the bioscourced yarn.

7.2. Whiteness

The bioscourced yarn shows some improvement over the grey yarn but is not equal to that of the Solomatic bleached grey yarn. However, the bioscourced cotton yarn and fabric have high absorbency and so these materials can be dyed in medium and deep shades without undergoing any bleaching pre-treatment. A considerable saving in the processing cost can thus be achieved due to reduction in cost of the bleaching chemicals and energy as well as the processing time.

7.3. Tenacity

The results are not conclusive but it may be safely concluded that the strength of the bioscourced and the bioscourced and bleached with only 25% of the usual quantity of hydrogen peroxide is higher than that of the commonly prepared cotton goods.

The pectinase scoured cotton materials have an economic potential because the process offers the advantages of lower consumption and so the lower cost of hydrogen peroxide and ancillary chemicals and possibly reduction in loss of weight of the material.

Saving in the weight of the finished products is of great importance to the towel and bed sheet manufacturers because weight is an important factor in the sale-value of their products. In addition to these, a major advantage is the lower cost of treatment of the effluent that has a relatively lower BOD and COD and alkalinity.

Actually if the bioscourced effluent could be collected separately before treatment with the peroxide, this water can be used for agricultural purposes. This may be an important consideration for the water-stressed countries like India and Pakistan where this effluent, rich in the organic nutrients (fertilizer), can be used for growing the ‘organic food’ after a minor treatment process. However, for using the effluent for agricultural purposes, the sequestrant to be used should be a biodegradable one and not the commonly used EDTA.

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References