Wet pretreatment of linen by enzyme and alternative bleaching techniques

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An attempt has been made to scour linen with a multifunctional cultured enzyme containing pectinase and xylanase. The activity level of the individual component in the enzyme is measured and then the optimum level of treatment is obtained. The removal of impurities is measured in terms of methylene blue absorption, residual lignin and absorbency. Bleaching with peroxide using sodium persulphate as activator has also been attempted along with scouring as well as a separate process. Combined scouring - bleaching although does not yield very good whiteness, the two-step pretreatment gives satisfactory results. Bleaching with KMnO₄ is also effectively done but with relatively higher strength loss. For ease in interpretation, the results are analysed with polar diagrams.

Keywords: Bleaching, Enzyme, Linen, Pectinase, Wet pretreatment, Xylanase

1 Introduction

Linen, known to be one of the oldest fibres, has acquired significance only in the recent times for apparels, especially as summer wear. It is extracted from flax, originating under bast category. The popularity of linen fabric among fashion designers has stimulated demand for increased quantities of the fibre1. The freshness, comfort and grace the linen garment offers, make the fibre special. However, from 1950s to 1980s, linen suffered lack of research, due to rapid expansion of synthetic industries2. With the revival in consumer demand, research has picked up in some of its manufacturing and processing aspects.

Regarding the wet processing of linen, pretreatment is one area of focus. Linen, like cotton has cellulose as its major component. Other than impurities like pectins, fats and waxes, it contains hemicellulose and lignin in significant quantity, the latter being a major hurdle in achieving good whiteness. Use of substrate specific enzymes has been attempted by researchers for impurities removal from linen with reasonable success3-4. This is an alternative to conventional chemical scouring with added advantage of low energy consumption and less effluent generation. As regards bleaching, hydrogen peroxide is universally used for all textile fibres. Since it is a high temperature process, efforts have been made especially on cotton to have a low temperature bleaching using activators. Use of activators like persulphates, tetraacetylene-diamine, nonyloxybenzene sulphonate for low temperature peroxide bleaching has been reported for last many years5-10. Persulphates, specifically dipersulphates are strong oxidants, typically manufactured as the sodium, potassium and ammonium salts. The standard oxidation – reduction potential of persulphate anion is 2.1 V and is also capable of inducing free radical reaction. Bleaching of cotton using KMnO₄ has also been worked on, permanganate being a strong oxidant11.

In the present work, a laboratory cultured enzyme containing both pectinase and xylanase has been used for scouring linen to remove the corresponding impurities, pectin and xylan i.e. hemicellulose. Since lignin is thoroughly attached to xylan, it is also expected to get removed. At the same temperature peroxide bleaching using sodium persulphate as activator has been carried out to see its effectiveness on linen. A few trials with hydrogen peroxide by conventional method and room temperature bleaching by KMnO₄ are also made.

2 Materials and Methods

2.1 Materials

Grey linen fabric of 1×1 plain weave, yarn count 28x32s, reeds/inch 42, picks /inch 52, and weight 195 g/m² was used for the study. The enzyme used was a laboratory cultured multifunctional enzyme with activity level of 30 IU/mL pectinase and 60 IU/mL xylanase. The laboratory reagent grade...
chemicals used were sodium hydroxide, phenol, sodium potassium tartrate, sodium meta bisulphate, dinitrosalicylic acid, hydrogen peroxide (50%), sodium persulphate, potassium permanganate, soda ash, trisodium phosphate, glacial acetic acid and common salt, while commercial grade desizer (Bactosol HTN) and peroxide stabilizer (Stabilizer AWNI) from Clariant were used.

2.2 Methods
The grey fabric was first desized using 2g/L Bactosol HTN along with common salt and non-ionic detergent 1g/L each. A pH of 6-6.5 was maintained using acetic acid. The treatment was given at 80°C (operating temperature for the thermo resistant enzyme) for 1 h, maintaining an MLR of 1:40 followed by thorough hot wash and cold wash. It was then dried in an oven at 60°C. The desizing effect was confirmed using a Tegewa scale.

2.2.1 Enzymatic Scouring
The enzyme was first tested for its activity using the standard test method given subsequently in section 2.2.4. This enzyme with 30 IU/mL pectinase and 60 IU/mL xylanase, after suitable dilution, was applied on small desized linen samples, at varying concentration and pH. One IU (International Unit) of enzyme activity is defined as the amount of enzyme that catalyzes the release of 1 µmole of reducing sugar equivalent to the corresponding substrate per minute under standard assay conditions. Since the optimum pH of the characterized enzyme was about 9, two pH values of 8.5 and 9.5 were chosen for treatment to check tolerance. After due preliminary trials, the concentration of pectinase was varied from 1.5 IU/mL to 12 IU/mL, while the corresponding strength of xylanase was automatically double of this, due to its strength in the enzyme solution itself. All the treatments were given in shaker bath at 50-55°C for 60 min, maintaining MLR at 1:40. On completion of the process, the samples were given thorough hot wash and cold wash.

2.2.2 Low Temperature Bleaching
The enzyme treatment after optimization was carried out at 10 IU/mL pectinase and 20 IU/mL xylanase at pH 9 with rest of the parameters remaining the same. Low temperature peroxide bleaching was carried out in same step as well as separate unit operation using sodium persulphate as activator. Hydrogen peroxide of 5, 10 and 15 g/L with corresponding persulphate concentrations of 2, 4 and 6g/L were used. In the separate scouring and bleaching process, the treatment was in one bath but in two steps, keeping the temperature and pH same all through.

2.2.3 Bleaching after Enzyme Treatment with known Oxidants
The same enzyme treatment was repeated for 6, 9 and 12 g/L pectinase (12,18 and 24 g/L xylanase correspondingly) and in the same bath peroxide bleaching at 80-85°C was carried out using the following recipe maintaining a pH of 10-11:

\[ \text{H}_2\text{O}_2 \ (50\%) \quad : \quad 10 \ g/L \]
\[ \text{Stabilizer AWNI} \quad : \quad 2 \ g/L \]
\[ \text{Trisodium phosphate} \quad : \quad 5 \ g/L \]
\[ \text{Soda ash} \quad : \quad 2 \ g/L \]

Other than this, one peroxide bleached sample was further bleached with potassium permanganate (KMnO₄) using 3 g/L oxidant at room temperature for 2 h. Acidic pH was maintained using 1 g/L acid (a mixture of acids having ratio 3:1 v/v sulphuric acid and acetic acid). One enzyme treated sample was also bleached with KMnO₄ directly. After the 2 h treatment, the fabric was washed in running water and treated with 4 g/L oxalic acid for 30 min at 85°C. Finally, the sample was rinsed in boiling water for 1 min and then dried.

2.2.4 Test Methods
The cultured enzyme was tested for the activity level of pectinase and xylanase by the standard procedures for assaying. To 0.5 mL of the suitably diluted test solution, 1.5 mL of dinitrosalicylic acid solution was added. The test tubes containing these were heated in boiling water for 15 min. On cooling, the optical density was measured at 540 nm in the Perkin Elmer UV spectrometer, against blank solution. The enzyme activity was determined from the following formula:

\[
\text{Enzyme activity (IU/mL)} = \frac{x \times \text{Dilution factor} \times 1000}{\text{Incubation time} \times \text{Volume of enzyme sample taken} \times \text{Mol.wt}}
\]

where \( x \) is the concentration derived from the optical density (O. D) values using Beer Lambert law for corresponding substrate. Dilution factor is the number of times enzyme is diluted while mol. wt of pectin is 212 and that of xylan is 150. The dinitrosalicylic acid solution was prepared by taking
5g NaOH, 1g phenol, 100 g sodium potassium tartarate, 0.25 g sodium metabisulphite and 5 g dinitrosalicylic acid (DNS) and then making the volume to 500 mL with distilled water.

Methylene blue exhaustion as a measure of presence of acidic impurities like pectic acid from pectin was determined, by treating 0.2 g fabric sample with methylene blue (CI Basic Blue 9) dye solution of 0.25% owf. This was done with occasional stirring at room temperature for 24 h at pH 8-8.5 using soda ash at an MLR of 1:50. The optical density (OD) of dye solution was measured both before and after treatment, with suitable dilution. Considering the former to be OD₁ and the latter to be OD₂, the exhaustion % was calculated using the following formula:

\[
\text{Exhaustion} \% = \left( \frac{\text{OD}_1 - \text{OD}_2}{\text{OD}_1} \right) \times 100
\]

The estimation of lignin was carried out by a process based on TAPPI standard test method 222-0S-74. For improvement in whiteness, whiteness index in Hunter system and yellowness index in ASTM E313 standard were measured on a Macbeth computer colour matching system with D65 illuminant and 10° observer. The tensile strength tests were carried out on Good Brand’s strength tester.

3 Results and Discussion

3.1 Action of Enzyme on Substrate

The enzyme when applied at very low strength of pectinase and xylanase, is not effective as evident from the high values of absorbency time, Methylene blue exhaustion % and residual lignin content shown in Table 1. This can be attributed to insufficient quantities of the enzyme, as at higher concentrations of the enzyme the absorbency is less than 3 s, while the residual pectin and xylan contents are also lower. At and above the activity levels of 3 IU/mL pectinase and 6 IU/mL xylanase, the pectinase is likely to act on pectin and decreasing the galacturonic acid content in treated linen thus giving less of methylene blue absorption, which is dependent on the presence of acidic group in substrate. Correspondingly, xylanase acting on xylan, removes the lignin associated with xylan, thus lowering the residual lignin content. The trends are similar in both the pH values of 8.5 and 9.5, indicating that variation of pH in this range is not making any difference and hence for subsequent trials, a pH of 9 (+/-0.5) is used. Also, beyond a strength of 9 IU/mL pectinase (18 IU/mL xylanase) there is no significant improvement in content of impurities removal. The water absorbency values are also found to be quite good except at the lowest activity levels of the enzymes taken. Imparting absorbency being one of the main objectives of scouring, the enzymatic treatment can be stated as an effective process for linen.

3.2 Enzymatic Scouring and Low Temperature Bleaching

The enzymatic scouring and bleaching was carried out both by one step process as well as two separate processes. In single step process, the whiteness obtained is not of a very high order, due to the non removal of natural impurities to desired level and

<table>
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<tr>
<th>Sl No</th>
<th>pH</th>
<th>Pectinase conc., IU/mL</th>
<th>Xylanase conc., IU/mL</th>
<th>Absorbency s</th>
<th>Methylene blue exh., %</th>
<th>Residual lignin, %</th>
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could also be attributed to interference in action of principal agents. The methylene blue exhaustion values and residual lignin contents being high in all the cases, indicate that the enzymatic scouring process is not effective in the given condition. Moreover, relatively high yellowness index values for all the three concentrations of peroxide and persulphate (Table 2) show that the bleaching results are not quite satisfactory.

Enzyme treatment followed by persulphate activated peroxide bleaching at the same temperature however gives promising results. As evident from the table, the removal of pectin is indicated by low methylene blue absorption values, similar to that obtained when only enzymatic scouring was carried out earlier. An appreciable quantity of lignin removal shows the effective action of xylanase component as well. Moreover, subsequent bleaching at 55°C complements well with the preceding enzyme giving reasonably high WI and low YI. The strength loss is also quite low as expected. Thus, the enzymatic scouring followed by low temperature bleach appears to be a useful option for linen pretreatment.

3.3 Enzymatic Pretreatment and Bleaching with \( \text{H}_2\text{O}_2 \) and \( \text{KMnO}_4 \)

Conventional peroxide bleaching preceded by 6, 9 and 12 IU/mL pectinase (corresponding xylanase being 12, 18 and 24 IU/mL) treatment, results in good impurities removal in terms of residual pectin and lignin in substrate. The whiteness, yellowness and strength loss values are quite encouraging. The whiteness of these samples are similar to that of the low temperature activated bleaching. The impurities removal does not significantly vary with enzyme strength, one reason for which could be subsequent high temperature alkaline treatment during peroxide bleaching. Permanganate bleaching after the peroxide bleaching yields the best whiteness result as shown in Table 3. The corresponding yellowness index is also very less. Treatment with only \( \text{KMnO}_4 \) on enzyme treated sample gives good whiteness, even better than peroxide. However, the strength loss is high in all the processes involving permanganate, probably due to the use of mineral acid in bleaching.

### 3.4 Polar Diagram Analysis

Polar diagrams for the various pretreatments involving the enzyme developed and hydrogen peroxide with and without aids are drawn for better visual assessment of their comparative performance under varying conditions. To draw the polar diagrams, the highest and lowest values of each measured parameter (or property) are assigned values 1 and 0 respectively when a higher value of the parameter is considered beneficial, and 0 and 1 respectively when a lower value is beneficial. Accordingly, the actual value of any parameter (property) has been assigned a value between 0 and 1 using the following relationship when higher value is desirable.

\[
\text{Assigned value} = \frac{\text{Actual value} - \text{Minimum value}}{\text{Maximum value} - \text{Minimum value}}
\]

In case, lower value is considered to be desirable, then

### Table 2—Enzyme scouring and persulphate assisted bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{H}_2\text{O}_2 ) conc. (g/L)</th>
<th>Persulphate conc. (g/L)</th>
<th>Methylene blue exh., %</th>
<th>Residual lignin, %</th>
<th>WI</th>
<th>YI</th>
<th>Strength loss, %</th>
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<td>S₁</td>
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<td>2.30</td>
<td>68.3</td>
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<tr>
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<td>40.36</td>
<td>2.14</td>
<td>67.9</td>
<td>19.2</td>
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<tr>
<td>S₃</td>
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<td>73.7</td>
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<td>D₂</td>
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<tr>
<td>D₃</td>
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<td>34.15</td>
<td>1.40</td>
<td>80.3</td>
<td>11.2</td>
<td>11.0</td>
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</table>

### Table 3—Enzyme scouring followed by peroxide/permanganate bleaching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pectinase conc. (%)</th>
<th>Xylanase conc. (%)</th>
<th>( \text{H}_2\text{O}_2 ) g/L</th>
<th>KMnO₄ g/L</th>
<th>Methylene blue exh., %</th>
<th>Residual lignin, %</th>
<th>WI</th>
<th>YI</th>
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<td>E₅</td>
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<td>20</td>
<td>-</td>
<td>3</td>
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<td>81.1</td>
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<td>17.9</td>
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</table>
Actual value – Minimum value
Assigned value = 1 – \frac{\text{Actual value} – \text{Minimum value}}{\text{Maximum value–Minimum value}}

The polar diagrams of the enzyme scour and different bleach effects are discussed hereunder.

3.4.1 Interpretation for Enzyme Scouring and Activated Bleach

The polar plots (Fig. 1) clearly indicate that the two step preparatory process (connoted as \(D_1, D_2, D_3\)) gives better results than the corresponding single step process \((S_1, S_2, S_3)\). Out of these, \(D_2\) and \(D_3\) show results close to each other. However, \(D_2\) may be considered to be the optimized one, due to use of peroxide and persulphate in reasonable quantities in the process.

3.4.2 Interpretation for Enzyme Scouring followed by Chemical Bleach

The comparative results show high whiteness values in the processes involving \(\text{KMnO}_4\) (samples \(E_4\) and \(E_5\)). The other attributes like yellowness index and residual lignin are also better than the conventional peroxide bleaching. Of the trials taken (Fig. 2), the two step bleaching yields the best values in terms of bleach effect although at the cost of strength.

3.4.3 Optimization of Pretreatment

Two processes are short listed, one a two stage enzyme scouring followed by persulphate assisted peroxide bleaching (sample \(D_2\) in Table 2), while the other is enzyme scouring with conventional peroxide bleaching followed by \(\text{KMnO}_4\) treatment (sample \(E_2\) of Table 3). Based on their assigned values relative to the whole set of experiments, the polar diagram (Fig. 3) is made. The plot gives a fair representation of the two except for the high strength loss in case of double bleach. The results are otherwise balanced in both the cases. The advantage with the first process is that it is carried out at a constantly low temperature of 55°C all through, thereby saving energy. The second one has the merit of the best whiteness, but the disadvantage is obviously the strength loss and long process time. Hence, in all, the enzymatic scouring followed by activated peroxide bleaching with optimum concentration of bath ingredients is a good choice for pretreatment of linen.

4 Conclusion

Linen, being more like cotton, can be pretreated in different ways, similar to that of cotton. In place of
conventional process, scouring can be effectively carried out on linen just like bioscouring of cotton. The enzymatic scouring followed by a low temperature peroxide bleaching using activator appears to be an effective process as far as wet pretreatment of linen is concerned. The low temperature bleaching gives results comparable to that of the conventional peroxide bleach. Hence, the enzyme scouring followed by activator assisted bleaching is a viable option for linen pretreatment. An excellent whiteness obtained by conventional peroxide treatment followed by permanganate bleach is however associated with low strength retention.

References