Effect of bio-carbonization of coarse wool on its dyeability

H El-Sayed¹, L El-Gabry & F Kantouch

Textile Research Division, National Research Centre, Dokki, Cairo, Egypt

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A mixture of acid cellulase, acid pectinase and xylanase has been utilized for removing vegetable matters from lightly contaminated Egyptian wool fleece. The proposed mixture is found to be effective in removing almost all the impurities based on cellulose, pectin and lignin without attacking wool keratin or affecting its inherent chemical and mechanical properties. The effect of bio-carbonization of wool on its dyeability with acid and 1:1 metal complex dyes has been studied. Kinetic studies as well as the fastness properties of the dyed fibres to washing and perspiration have also been reported. The properties of bio-carbonized wool fibres are found to be better than those of wool fibres carbonized by conventional method using sulphuric acid.

Keywords: Bio-carbonization, Cellulase, Dyeability, Enzyme treatment, Pectinase, Wool, Xylanase

1 Introduction

Raw wools are contaminated with various amounts of vegetable matters (VM) depending on the breed of sheep. These vegetable matters include burrs, seeds, grass, and straw¹. Up to 8.5 % of raw wool fibres contents are vegetable contaminants. This implies that the contamination with vegetable material is too high for successful removal mechanically and that a more drastic chemical treatment is essential², ³.

Carbonization of wool involves removal of VM and skin flakes. The principle of this process is to use a strong acid, namely sulphuric acid, to transform cellulose into the easily removable hydrocellulose. Replacement of chemical carbonization by enzymes, such as cellulases and xylanase, has been investigated with a view to reducing wool fibre damage, effluent load and energy consumption⁴, ⁵. In 1998, the Institute of Natural Fibres of Poland announced the Biocarbo process. It is a biological method of cleaning wool from vegetable impurities and is based on the use of biologically active preparations containing pectolytic and cellulolytic enzymes with small amount of certain chemicals⁶. Similarly, after incubating wool with cellulases, burr removal became easier due to weakening of cohesion between burrs and wool⁷. No chemical or physical damage of the wool was observed after mechanical removal of the enzyme-treated burrs.

The present work aims at utilizing some commercially available enzymes for the treatment of raw Egyptian wool and studying the effect of bio-carbonization treatment of wool on its dyeability using acid and 1:1 metal complex dyestuffs.

2 Materials and Methods

2.1 Materials

Egyptian wool fleece (Barki) was purchased from the Oriental Weavers Company, Egypt. The main fibre length is 72 mm and main fibre diameter is 41 µm. The fibres were used as such without any purification.

A commercial acid cellulase Biotouch L (AB Enzymes; formerly Röhm Enzyme Darmstadt, Germany) was used. It contains both exo- and endo-glucanases (E.C. 3.2.1.4)⁸. Acid pectinase (E.C. 3.2.1.15) was supplied from Fluka, Steinheim, Germany. Its reported activity is 1 U/mg. Xylanase from bacteria (E. C. 3.2.1.8) was supplied by Fluka, Steinheim, Germany. Xylanase preparations have been used to degrade lignin for many purposes⁹, ¹⁰.

Egyptol⁰ PLM, a nonionic detergent based on nonyl phenol ethoxylate, was supplied from Starch and Detergent Company, Alexandria, Egypt. Other chemicals used were of laboratory grade.

Acid Fast Red EG (C. I. Acid Red 1) from Bayer, Leverkusen, Germany, and 1:1 metal complex dye,
Neolan® Red P from Huntsman Textile Effects, Basel, Switzerland, were used in this study.

2.2 Methods of Treatment

2.2.1 Scouring

The raw greasy wool was scoured to remove suint, dirts and soluble impurities. Scouring was carried out in the laboratory using 1 g/L Egyptol® PLM in presence of 1 g/L sodium carbonate as a builder to facilitate removal of contaminants. Scouring of wool was carried out at 50 °C for 30 min with occasional shaking, maintaining wool-to-liquor ratio (L.R.) at 1:40 (owf). Wool fibres were then thoroughly washed with hot water and finally dried at 105 °C for 1 h.

2.2.2 Calculation of Vegetable Matters in Raw Wool

The wet scoured wool was transferred to a sintered glass crucible G1 and the residual scouring solution was taken out by suction. The wool sample was then washed several times using hot water followed by complete suction to remove the residual washing water. The wool sample was then dried at 105 °C for 1 h. The dried scoured wool was subjected to a repeated carding and combing processes to get rid of the contaminating vegetable matters. The removed vegetable matters were collected and accurately weighed. The content of vegetable matters in wool was calculated using the following relationship:

\[
\% \text{ Vegetable matters content} = \left( \frac{W_b - W_a}{W_a} \right) \times 100
\]

where \(W_a\) is the weight of wool fibre before removing VM; and \(W_b\) the weight of wool fibres after removing VM.

In another experiment, the amount of vegetable matters in wool was assessed chemically by dissolving the scoured wool in 5% sodium hydroxide solution for 5 min at the boil or in sodium hypochlorite solution for 30 min at room temperature.

2.2.3 Carbonization of Wool Fibres

Scoured wool fibres were carbonized according to the conventional method using sulphuric acid solution (4.5–7.5 %) followed by drying and baking.

2.2.4 Enzymatic Treatment of Wool Fibres

Scoured wool fibres containing VM were treated separately with the acid cellulase (Biotouch L), acid pectinase or xylanase (1–20 mL/L) at pH 5 (using acetate buffer) and 50 °C for different periods of time (60–210 min) with occasional shaking. The wool-to-liquor ratio was maintained at 1:25. The enzyme-treated wool sample was then washed and dried. The hydrolyzed brittle vegetable matter was taken out by beating or carding. In another investigation, different mixtures of the aforementioned enzymes were applied to the scoured wool at 50°C for 120 min using pH 5 and wool-to-liquor ratio 1:30.

2.3 Test Methods

The loss in weight of the wool sample after each enzymatic treatment was assessed using the following formula:

\[
\% \text{ weight loss} = \left( \frac{W_1 - W_2}{W_1} \right) \times 100
\]

where \(W_1\) and \(W_2\) are the weights of untreated and enzyme-treated samples respectively.

The tenacity and elongation-at-break of raw, enzyme-treated and carbonized wool using the traditional acid method were measured according to ASTM standard method D1 445-95 2002 using Stelometer tester (Spinlab AG Model 154M, Germany).

The alkali solubility of the untreated as well as the enzyme-treated or acid-carbonized wool fibres was evaluated treated using the standard method (ASTM D 1283-85). The alkali solubility per cent of wool was calculated using the following relationship:

\[
\% \text{ Alkali solubility} = \left( \frac{W_4 - W_3}{W_4} \right) \times 100
\]

where \(W_4\) is the weight of dry sample; and \(W_3\), the weight of dry wool residue.

2.4 Dyeing of Wool Fibres

2.4.1 Dyeing Method

Dyeing of raw, carbonized and bio-carbonized wool fibres was carried out using 2% (owf) of Acid Red 1 at 85 °C using pH 4.5 and liquor ratio 1:100 in presence of 1 g/L Egyptol® PLM. Aliquots of the dyeing bath were taken for determination of the extent of dye exhaustion after different periods; the dye exhaustion was estimated by spectrophotometric method.

Wool sample was also dyed with 2% (owf) metal complex dye Neolan® Red P at 85 °C for 150 min using pH 3.5 and liquor ratio 1:100 in presence of 1 g/L Egyptol® PLM. The dyed fibres were rinsed thoroughly with running water and air dried. The per cent of dye exhaustion was estimated by spectrophotometric method.
2.4.2 Dyeing Properties

Measurement of the residual dye in the dyeing bath (dye exhaustion) was determined spectrophotometrically using JENWAY-6405 U/V spectrophotometer. In another experiment, the dyed fibres were extracted with a hot mixture (1:1) of dimethyl formamide/water and the amount of the extracted dye was determined spectrophotometrically.\(^{11}\)

The time of half dyeing \((t_{1/2} \text{ min})\) was determined by dyeing 5 g of wool sample with 2\% dye \((\text{owf})\) both at 85ºC and 95ºC. Each set included dyeing for different time intervals between 5 min and 150 min. Samples were removed from the dyebath immediately after the prescribed dyeing time and the amount of remaining dye in the liquor was determined spectrophotometrically.\(^{12}\) For each dyeing temperature, the percentage exhaustion was plotted against dyeing time and the time of half dyeing was determined from these plots.

The specific dye rate constant \((K')\) is estimated using the following equation\(^{13}\):

\[
K = 0.5 \frac{C_\infty}{d} \left( \frac{d}{t_{1/2}} \right)^{1/2}
\]

where \(d\) is the fibre diameter \((\text{cm})\); and \(C_\infty\), the amount of dye taken up by the fibre at equilibrium conditions.

Samples of the examined fibres (5 g) were dyed in dye solution (500 mL) for 6 h. The amount of dye taken up by the fibres \((C_\infty)\) was determined spectrophotometrically. Another dyeing test was performed for a short period (10 min) and \(C_t\) was similarly determined. The values of \(C_t/C_\infty\) were calculated and the apparent diffusion coefficient \((D)\) could then be calculated using Hill's equation, as shown below:

\[
D, \text{cm}^2s^{-1} = \frac{C_t}{C_\infty} \times \frac{d^2}{T} \times 100
\]

where \(d\) is the diameter of the fibre in \(\mu\text{m}\); and \(T\), the absolute temperature.

2.4.3 Fastness Properties

The colour fastness of the dyed wool fibres to washing was determined according to the AATCC test method 61–1075 using a laboratory laundrometer.\(^{14}\) Fastness to perspiration test was carried out in either acidic or alkaline solution according to the AATCC technical manual 69, 23\,(1993)\(^{13}\). For fastness to respiration (alkaline solution) test, histidine monohydrochloride monohydrate solution (0.25 g/L), sodium chloride (10 g/L), and sodium dihydrogen phosphate (1 g/L) were dissolved in one litre of distilled water. Finally, the pH of the prepared solution was adjusted to 8 by the use of 0.1 sodium hydroxide solution. For fastness to perspiration (acidic solution) test, histidine monohydrochloride monohydrate solution (0.25 g/L), sodium chloride (10 g/L), and sodium dihydrogen phosphate (1 g/L) were dissolved in one litre of distilled water. The pH of the prepared solution was adjusted to 4.3 by 10\% of acetic acid solution.

3 Results and Discussion

3.1 Effect of Single Enzyme Treatment

Removal of vegetable impurities (i.e. cellulose, pectin and lignin) from raw wool was carried out using selected cellulose, pectin and lignin digesting enzymes. This method was compared with the traditional carbonization process which utilises dilute sulphuric acid. The findings are shown in Table 1.

Treatment of raw wool fibres with sulphuric acid results in almost complete removal of the vegetable matters from wool. However, the tensile strength of the carbonized fibre decreased by about 25.7\%, relative to raw wool fibres; presumably due to partial peptide bond hydrolysis during this process.\(^{15}\) Mizell et al.\(^{16}\) have reported that the carbonization of wool with sulphuric acid results in extensive fibre breakage in subsequent processes. Zahn\(^{17}\) has monitored some further damage when the carbonized wool is not promptly rinsed and neutralized.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Enzyme conc. mL/L</th>
<th>Impurities content, %</th>
<th>Tensile strength cN/tex</th>
<th>Alkali solubility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>-</td>
<td>4.00</td>
<td>13.88</td>
<td>11.6</td>
</tr>
<tr>
<td>Carbonized</td>
<td>-</td>
<td>0.10</td>
<td>10.45</td>
<td>12.3</td>
</tr>
<tr>
<td>Biotouch L</td>
<td>1</td>
<td>2.02</td>
<td>13.70</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.82</td>
<td>14.01</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.44</td>
<td>14.04</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.09</td>
<td>14.00</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.05</td>
<td>14.08</td>
<td>11.6</td>
</tr>
<tr>
<td>Acid pectinase</td>
<td>1</td>
<td>2.48</td>
<td>13.85</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.32</td>
<td>13.87</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.05</td>
<td>13.88</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.77</td>
<td>13.92</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.20</td>
<td>13.94</td>
<td>12.0</td>
</tr>
<tr>
<td>Xylanase</td>
<td>1</td>
<td>2.61</td>
<td>13.86</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.46</td>
<td>13.88</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.31</td>
<td>13.95</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.12</td>
<td>13.92</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.73</td>
<td>13.92</td>
<td>11.5</td>
</tr>
</tbody>
</table>
There is a limited increase in the alkali solubility of the wool fibres carbonized with sulphuric acid. This may be attributed to the partial reaction of sulphuric acid with wool under the effect of the drying conditions. This may lead to formation of sulphonic or sulphate groups which increase the extent of alkali solubility\(^{15}\).

Treatment of raw scoured wool fibres with cellulase, acid pectinase or xylanase removes the VM from wool to various extents, depending on the nature and amount of the enzyme used. The amount of remaining VM (1.05%) is about 25% of the total impurity content of raw wool in case of using 20 mL/L Biotouch L. This is, presumably due to the specificity of the used enzymes; Biotouch L attacks cellulosic impurities, acid pectinase degrades pectin, and xylanase removes lignin. Limited increase in the tensile strength was monitored when wool fibres were treated with high concentrations (5–20 mL/L) of cellulase or pectinase enzyme.

The alkali solubility of the enzyme-treated fibres was not significantly altered compared to raw wool. Again, this could be attributed to the specificity of the used enzymes which attack only the VM away from wool keratin; an advantage of enzymes over sulphuric acid in removal of VM from wool\(^{18}\).

### 3.2 Effect of Mix Enzyme Treatment

In another experiment, scoured wool fibres were treated with mixture of Biotouch L, acid pectinase and xylanase at the appropriate pH and temperature. The effect of treatment of wool with this mixture of enzymes is shown in Table 2.

The synergetic action of the three enzymes in one bath is found to be much more effective in removing the VM from raw wool than using individual or binary enzyme system. The per cent of VM in wool is reduced from 4 in case of raw wool to 0.16 in case of wool fibres pretreated with mixture of the three enzymes. This may be attributed to the ability of each enzyme to remove a definite part of the VM that contaminates raw wool. Biotouch is able to degrade cellulose and hemicellulose, acid pectinase degrades pectin, and xylanase removes lignin.

### 3.3 Effect of Treatment Time

In an attempt to decrease the treatment time and hence the cost of the biocarbonization process for wool, raw wool was treated with a mixture of cellulase, acid pectinase and xylanase for different periods of time. Table 3 shows that as the treatment time of wool with the enzymes increases up to 120 min, the impurities content in the treated fibres decreases. Further increase in the treatment time has no significant effect on the extent of removal of VM as well as the tensile strength and alkali solubility of the treated sample.

### 3.4 Dyeing Characteristics

Untreated wool fibres as well as those pretreated with mixture of cellulase, pectinase and xylanase enzymes were dyed with Acid Fast Red EG or 1:1 metal complex dye at 85ºC and 95ºC separately for various periods of time and the dye exhaustion percentages were determined. Figures 1 and 2 show the effect of dyeing time on the dye exhaustion percentage.

It is observed that scouring of wool led to remarkable increase in the dye exhaustion with either acid or metal complex dye at both temperatures. This is, presumably, due to the removal of greasy matters.

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### Table 2—Effect of treatment of raw wool with mixture of enzymes on its properties

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Impurity content %</th>
<th>Tensile strength, cN/tex</th>
<th>Alkali solubility %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>4.00</td>
<td>13.88</td>
<td>11.6</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>0.10</td>
<td>10.45</td>
<td>12.3</td>
</tr>
<tr>
<td>Biotouch L</td>
<td>1.05</td>
<td>14.08</td>
<td>11.6</td>
</tr>
<tr>
<td>Acid pectinase</td>
<td>1.20</td>
<td>13.94</td>
<td>12.0</td>
</tr>
<tr>
<td>Xylanase</td>
<td>1.73</td>
<td>13.92</td>
<td>11.5</td>
</tr>
<tr>
<td>Biotouch L + acid pectinase (1:1)</td>
<td>0.78</td>
<td>13.99</td>
<td>12.3</td>
</tr>
<tr>
<td>Biotouch L + xylanase (1:1)</td>
<td>0.87</td>
<td>13.96</td>
<td>11.6</td>
</tr>
<tr>
<td>Acid pectinase + xylanase (1:1)</td>
<td>1.05</td>
<td>13.89</td>
<td>11.6</td>
</tr>
<tr>
<td>Biotouch L + acid pectinase + xylanase (1:1:1)</td>
<td>0.16</td>
<td>14.12</td>
<td>12.6</td>
</tr>
</tbody>
</table>

### Table 3—Effect of time of treatment of raw wool with mixture of enzymes on its properties

<table>
<thead>
<tr>
<th>Enzyme mixture (Biotouch L + acid pectinase + xylanase)</th>
<th>Time, min</th>
<th>Impurity content, %</th>
<th>Tensile strength, cN/tex</th>
<th>Alkali solubility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>-</td>
<td>4.00</td>
<td>13.6</td>
<td>11.6</td>
</tr>
<tr>
<td>Sulphuric acid a</td>
<td>-</td>
<td>0.10</td>
<td>10.1</td>
<td>13.3</td>
</tr>
<tr>
<td>Enzyme mixture</td>
<td>60</td>
<td>1.81</td>
<td>13.5</td>
<td>11.8</td>
</tr>
<tr>
<td>(Biotouch L + acid pectinase + xylanase)</td>
<td>90</td>
<td>0.96</td>
<td>14.2</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>0.16</td>
<td>15.8</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.14</td>
<td>15.8</td>
<td>12.8</td>
</tr>
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<td></td>
<td>180</td>
<td>0.13</td>
<td>15.7</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>0.14</td>
<td>15.5</td>
<td>12.9</td>
</tr>
</tbody>
</table>

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*Wool fibre was padded with dilute solution of H\(_2\)SO\(_4\) (7% w/w, 65% pick-up), dried at 90 ºC to concentrate the acid, and finally baked at 125 ºC for 1 min.*
from wool under the influence of alkaline conditions used in scouring. This would likely increase the hydrophilicity of wool fibres and hence enhance its subsequent dyeing.

Biocarbonization of the pre-scoured wool with a mixture of cellulase, pectinase and xylanase led to further enhancement in its dyeability with acid as well as metal complex dyes at 85 °C. This may be attributed to the synergetic effect of the used three enzymes in removing the VM from raw wool. Owing to their non-protenic nature, any amount of VM presents in wool fibres leads to unleveled dyeing. These VM are not dyed with acid and metal complex dyes and hence reported as dye-hindering niches

Further increase in the dyeing temperature to 95°C led to limited improvement in the dyeability of the scoured and biocarbonized wool with acid and 1:1 metal complex dyes.

Treatment of the scoured wool with sulphuric acid led to appreciable decrease in its dyeability with the studied anionic dye. This can be attributed to sulphatation of some amino acids in wool keratin, like serine and threonine. These sites have been reported earlier as dye-resist niches for acid dyes.

3.5 Dyeing Kinetics

Table 4 shows the values of half dyeing time ($t_{1/2}$), specific dyeing rate constant ($K'$) as well as the diffusion coefficient (D) calculated for the raw, scoured, carbonized and biocarbonized wool fibres dyed with acid and metal complex dyes.

It is clarified that the half dyeing time of wool fibres decreases after scouring. Again, this is due to the enhancement in the wettability of wool after removing the hydrophobic greasy matters by scouring. Carbonization of the scoured wool by sulphuric acid has nearly no effect on $t_{1/2}$. In all cases, the lowest half dyeing time ($t_{1/2}$) is attained incase of biocarbonization of wool with mixture of enzymes.

It is also observed that the specific dyeing rate constant ($K'$) of wool fibres increases upon scouring, carbonization or biocarbonization of wool especially when dyeing was carried out at 85°C. The diffusion coefficient (D) of the dyed wool fibres increases in the case of enzyme-treated fibres as compared to the untreated one, depending on the nature of treatment. It can be observed that the
dyeing rate constant and the diffusion coefficient for the scoured wool fibres treated with mixture of enzymes are relatively higher than that of fibres treated with sulphuric acid.

### 3.6 Fastness Properties

The wash and perspiration fastness of the acid or metal complex dyed untreated as well as treated wool fibres are shown in Tables 5 and 6. It is observed that the fastness properties of wool fibres against washing and perspiration do not change remarkably after scouring, carbonization or biocarbonization. The results are nearly similar to that obtained on dyeing with Acid Red EG or Neolan Red P at both 85 °C and 95 °C.

### 4 Conclusions

The Egyptian wool fleece was successfully purified from vegetable matters by using a mixture of cellulase, pectinase and xylanase enzymes without affecting the inherent properties of wool. Being highly specific hydrolyzing agents, these enzymes do not cause any loss in both fibre weight and strength. For heavily contaminated wool fibres, these enzymes can be coupled with mechanical cleaning methods or even less aggressive chemical methods.
References