Improvement of enzymatic antifelting treatment of wool fiber and its effect on dyeing with juglone from a common walnut plant

Y Chemchame1,3, H Benzbir4, A Kachachi1, M El Bouchti2 and A Kharchafi1

1Department of Traditional Weaving, Academy of Traditional Arts, Foundation of Hassan II Mosque, Casablanca, Morocco.
2REMTEX Laboratory, High School of Industry Textile and Clothing (ESITH), PO Box 7731, Oulfa, Casablanca, Morocco.
3Author to whom any correspondence should be addressed

Abstract. The objective of this study is to assess an enzymatic effect on the antifelting treatment of yarn and wool fabric. Enzymes, namely, the proteases cardosines A and B, are extracted from the flowers of the cardoon (Cynara cardunculus L) plant. Several conditions of enzymatic treatment are studied in order to optimize the antifelting process and improve shrink proofing. The optimal process is at 40 °C for 2 h in an alkaline medium at pH 10. The results show that the shrinkage of 16.8% for untreated yarn is reduced to 0%, while the shrinkage of 10% for the untreated fabric is reduced to 5%. In addition, the antifelting treatment increases the dye absorbance of a walnut stain (common walnut plant) on the yarn and wool fabric, although the fixation dye rate is decreased. Post oxidation is tested in order to improve the fixation dye rate and the washing fastness of juglone on the wool yarn and fabric.

1. Introduction
Antifelting treatment is significantly important for improving shrink proofing and preserving fabric armor. After washing, the whole orientation of the fibers on the fabric surface is conserved, thereby maintaining the original look.

Several studies have confirmed the efficiency of bioantifelting treatment and have shown that it can replace the oxidant agents such as sodium hypochlorite and peroxy sulphuric, which can cause damage to the fibers and the environment. In the antifelting treatment of wool, cardosines were not used before this time or may be rarely. However, there were a lot of research in antifelting treatment with papain, savinase, cutinase, woolase, porcine trypsine and others. Nurhan and Merih studied enzymatic, hydrogen peroxide and sodium hypochloride, and the additive agents were based on polyurethane, polysiloxane, silicone, chitosan, a hydrophilic and a natural polymer oxidative, to improve the shrink-proofing and antifelting properties of wool. They performed the experiments with enzymatic treatments using commercial protease preparations, such as Perizym AFW, Alcalase 2.5 L, Savinase 16 L and Papain [1]. A biocomposite made from keratin polypeptides and waterborne polyurethane [2] was employed as a bioantifelting agent for wool fabric by Zhuang D. et al. [3]. Their results indicated that
with an increasing content of keratin polypeptides from 0 to 6 wt.%, the area shrinking rate of the treated wool fabrics decreased from 4.55% to 0.47% [3].

Using others technics, a significant improvement in the wettability of chlorinated and plasma-treated wool fabrics has been observed, when compared with an untreated fabric sample [4]. The improved hydrophilicity of the wool fiber surface by nitrogen plasma could enhance and achieve a better polymer deposition on the surface for improving the antifelting properties of wool when compared with the chlorination process [4].

In this research, we seek to achieve a new zero-AOX [5] antifelting processing alternative to conventional processes, such as chlorine-Hercosett processing, and thus, use environmentally-friendly enzymes extracted from plants [6]. We choose the cardoon plant (*Cynara cardunculus L*) as a source of protease enzymes known as cardosines. They can break the peptidic bonds between the hydrophobic amino acids of the protein [7]. The maximum effect of these enzymes can be achieved in acid conditions. There are two principal types of cardosines: cardosine A and cardosine B. Like chymosin, cardosine A is considered to be responsible for the coagulant activity of proteins, whereas cardosine B has proteolytic activity (Verissimo et al. 1996).

The aim of this work is to study the enzymatic effect on the antifelting treatment of the wool. Hence, we tested the antifelting effect on yarn and wool fabric using cardosines extracted from the cardoon flower (*Cynara cardunculus L*). Various treatment conditions are studied in order to establish the optimal recipe. Moreover, the effect of antifelting treatment on the dyed yarn and wool fabric is studied to improve the absorbance dye of juglone extracted from a walnut stain (common walnut plant) [8–10].

2. Experimental

2.1. Materials

2.1.1. Wool fiber features. The wool fiber was from the Timahdit region in Morocco. Brown fleece was compacted and homogenized into a medium-weight fleece of 1.9 kg and the fiber fineness was 44–50 using the Bradford scale, with a fiber medium length of 9.6 cm.

2.1.2. Enzymes. The enzymes were extracted from the flowers of the cardoon plant (*Cynara Cardunculus L*). This plant grows in several regions of Morocco. The extraction method was based on the maceration in distilled water during 24 hours (h) under cover and room temperature.

2.1.3. Natural dye. Juglone dye was extracted from the walnut stain of the common walnut plant, which grows in the north of Morocco [11]. The extraction method was based on water solubilizing at high temperature of the dried and powdered walnut stain. The dye extraction can be achieved by macerating in water at low temperature, as described below.

2.1.4. Chemicals. Alkali reagents, sodium carbonate (Na$_2$CO$_3$) and the acidic reagent, acetic acid (CH$_3$COOH), were of analytical grade and were from Sigma Aldrich (Germany). H$_2$O$_2$ was from Solvapur (Casablanca, Morocco). A Marseille soap-type was prepared from vegetable oil and was purchased from a supermarket.

2.1.5. Spectrophotometry. An ultraviolet-visible spectrophotometer (Thermo, Helios Epsilon) was used at 325–1100 nm, with a spectral bandwidth of 1 nm.

2.1.6. Bath. A 250 mL flask was used. Heating was carried out with a thermostat hotplate (Scilogex MS-H280-Pro).

2.2. Optimization of enzymatic treatment conditions

2.2.1. Enzymatic extraction. A mass of 90 g of fresh flower cardoon was macerated in 450 mL of distilled water for 24 h under cover at room temperature. The blend was filtered using filter paper that was used in the antifelting treatment.
2.2.2. Enzymatic treatment of wool yarn. Nine yarns of 1 g were placed separately in nine baths containing 50 mL of enzymatic extract and acetic acid at pH 5. The first three baths were heated at 40 °C and kept at this temperature for 1, 2 and 3 h, respectively. The second and third sets of baths were heated at 50 and 60 °C, respectively, and kept at these temperatures for 1, 2 and 3 h, respectively, as for the first three baths. At the end of the treatment process, the yarns were rinsed in cold water.

2.2.3. Enzymatic treatment of wool fabric. A mass of 3 g of wool fabric was placed in a bath containing 150 mL of enzymatic extract and acetic acid at pH 5. The bath was heated at 60 °C and kept at this temperature for 2 h.

2.2.4. Soaping test. The treated yarns and fabric were soaped with 1 g/L Marseille soap at 60 °C for 15 min and a liquid ratio of 1/50. The same soaping process was repeated three times in order to test the enzymatic antifelting treatment of the yarns.

2.3. Dyeing process of yarn and fabric with walnut stain extract

2.3.1. Preparation of extract dyes. A walnut stain of the common walnut plant (3 g) was stirred in 50 mL of water at 40 °C for 2 h, with 10 g of sodium carbonate added to reach pH 10. The solution was filtered using filter paper and well preserved for the dyeing phase.

2.3.2. Dyeing. Two yarn samples of 0.5 g and two fabric samples of 1.5 g, with one of them antifelted (yarn and fabric) as described above, were placed in a bath containing 50 mL and 100 mL of dye (extract prepared from 3 g of walnut stain in 50 mL of water), at 90 °C and pH 4 for 1 h at a ratio of 1/50 and 1/33, respectively.

2.3.3. Soaping. The dyed yarns were soaped with 0.5 g/L Marseille soap at 60 °C for 15 min and a liquid ratio of 1/50.

2.4. Post oxidation of antifelted yarn and fabric
The antifelted dyed yarn and fabric were placed in two baths containing 4 mL of peroxide hydrogen in 25 mL and in 37.5 mL of distilled water and acetic acid at pH 4 at 45 °C for 15 min.

2.5. Spectral analysis

2.5.1. Spectrophotometer calibration. Spectrophotometer calibration was achieved by using distilled water as a standard solution.

2.5.2. Measurement of dye exhaustion and fixation rate. One mL of solution was removed from each dye bath for measurement. Each sample of yarn and fabric was diluted to 20 and 30 mL, respectively, using distilled water. The absorbance measurements are shown in table 4. The absorbances were measured at 400 nm.

2.6. Washing fastness
The washing fastness was determined over 30 min at 40 °C, according to ISO 105-C6:A1S [12].

3. Results and discussion

3.1. Optimization of enzymatic treatment conditions
Table 1 shows the length variation of antifelted yarns after the soaping test. The initial length of the yarns is 127 cm.
Table 1. Measurement lengths (cm) of antifelted yarns at different temperatures and duration.

| Duration (h) | 40°C | 50°C | 60°C |
|--------------|------|------|------|
| 1            | 122  | 121  | 121  |
| 2            | 120  | 124  | 127  |
| 3            | 127  | 127  | 127  |

The optimal antifelting conditions were established at 60 °C for 2 h of treatment and heating at 40 °C for 3 h. These conditions can ensure the perfect shrinking resistance after three soaping operations.

3.2. Enzymatic treatment of wool yarn
Table 2 shows the length variation of antifelted and non-antifelted yarns after the soaping test.

Table 2. Dimensional measurements (cm) of antifelted (AF) and non-antifelted (NAF) yarns.

|                  | NAF yarn | AF yarn |
|------------------|----------|---------|
| Initial length (cm) | 113      | 127     |
| Final length (cm)   | 94       | 127     |
| Shrinking rate (%)  | 16.8     | 0.0     |

The treatment with the optimal conditions described above ensured a high shrinking-resistance to the wool yarn, compared to the non-treated yarn.

3.3. Enzymatic treatment of wool fabric
The fabric is the wool canvas, which prevents the mobility of fibers. In order to assess better the antifelting effect on this fabric, the enzyme quantity was increased and the soaping test was intensified.

Table 3 shows the length variation of antifelted and non-antifelted fabric after the soaping test.

Table 3. Dimensional measurements (cm) of antifelted (AF) and non-antifelted (NAF) fabric.

|                  | NAF fabric | AF fabric |
|------------------|------------|-----------|
| Initial dimensions (cm) | 10/10      | 10/10     |
| Final dimensions (cm)   | 9.5/9.5    | 9/9       |
| Shrinking proof (%)     | 5.0        | 0.0       |

As shown in table 3, the shrinking proof of antifelted fabric was lower than the non-treated fabric. This indicates that the intensified soaping test caused more important shrinking of the non-treated fabric.

3.4. Exhaustion and fixation dye rate in dye bath
The absorbances of the initial, final dye baths and residual Soaping bath are presented in table 4.

Table 4. Exhaustion and fixation rate of juglone in the dye bath.

|                  | Initial dye bath (cm) | Final dye bath (cm) | Exhaustion rate (%) | Residual Soaping bath | No fixed dye rate | Fixation rate ((Absi-Absf)/Absi)*100 |
|------------------|-----------------------|---------------------|---------------------|-----------------------|------------------|--------------------------------------|
| Absorbance on AF yarn | 1.795                 | 1.349               | 0.093               | 5.1%                  | 19.6%            |                                      |
The exhaustion dye rate on the antifelted yarn and fabric was higher than the non-antifelted yarn. This can be explained by the higher accessibility of the fiber to the dye, due to the partial destruction of the fiber scale. The effect of antifelting on the dye absorbance in fabric was not very important. As observed for the yarn, this can be due to the armor structure of the fabric, which is tight and dense.

The non-fixed dye rate was higher for the antifelted yarn than the non-antifelted yarn. This might be explained by some destruction of the active sites of the fiber.

3.5. Washing fastness after post oxidation

Measurements that were obtained for the antifelted dyed yarn and fabric are presented in table 5.

| Samples          | Washing fastness (assessing staining) | Washing fastness (assessing change in color) |
|------------------|--------------------------------------|---------------------------------------------|
|                  | WO (wool) | PAC (poly-acril) | PES (polyester) | PA (poly-amide) | CO (coton) | CA (cellulose acetate) |                  |
| Dyed yarn        | 4         | 4-5              | 4-5              | 4               | 4          | 4                        | 4-5              |
| Dyed yarn without PO | 4         | 4-5              | 4-5              | 4               | 4          | 4                        | 4-5              |
| Dyed fabric with PO | 3-4       | 3-4              | 4                | 4-5             | 4-5        | 4                        | 4-5              |
| Dyed fabric without PO | 3-4       | 3                | 3-4              | 4-5             | 4-5        | 3-4                      | 4-5              |

The values from these experiments confirm the solid fixation of dyes using the post oxidation. The washing fastness was improved on the dyed fabric, but still constant on the dyed yarn. The juglone colorant was converted to the non-soluble form inside the fiber after post oxidation. The good washing fastness on the dyed yarn was attributed principally to the high degree of hydrogens and Van der Waals bonds, established inside the fibers. Consequently, the post oxidation of dyed yarn did not influence the washing fastness.

4. Conclusions

The antifelting treatment with cardosine enzymes in the optimal conditions ensured a high shrinking-resistance to the wool yarn and fabric, compared to the non-treated yarn and fabric.

Also, the antifelting effect improved the dye absorbance on fabric, and more so on yarn. This improvement was due to the partial destruction of fiber scale, which increased the accessibility of the
fiber to the dye juglone. The structure of the fabric is tight and dense; hence, the dye absorbance was lower than those observed on yarn.

In addition, no fixed dye rate on the antifelted yarn was higher than for the non-antifelted yarn. This can be explained by some destruction of the active sites of the fiber. The post oxidation was confirmed for improving the washing fastness of dyed wool fabric. The juglone colorant was converted to the non-soluble form inside the fiber after post oxidation.

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