PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 2(2009), 1-6

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Improving Colorant Absorption from Pistachio Hulls on Wool Fiber Using Protease Enzyme

M. Parvinzadeh

Ph.D. Student, Department of Textile, Islamic Azad University, Shahre Rey Branch, P.O.Box: 18735-334, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 28-6-2008
Accepted: 6-12-2008
Available online:12-3-2009

Keywords:
Wool
Wool dyeing
Pistachio hulls
Enzyme
Fastness
Reflectance spectroscopy.

ABSTRACT

Nowadays, textile processing based on biotechnology has gained its importance in the view of stringent environmental and industrial safety conditions. The use of protease enzymes in protein fibers to improve some physical and mechanical properties is particularly interesting. In this research, wool yarns were first treated with different concentrations of protease enzymes in aqueous solution including 1%, 2%, 4% and 6% o.w.f. for 60 minutes. The dyeing process was then applied on the treated yarns with pistachio hulls as a fruit waste. Some of physical, mechanical and colorimetric properties of the treated wool yarns were discussed. Tensile strength of the treated yarns was decreased due to the enzyme treatment and it continued to decrease with an increase in the enzyme concentration in solution. Lightness was decreased for the samples treated with enzymes. The wash and light fastness properties of samples were measured according to ISO 105-CO5 and Daylight ISO 105-BO1. The washing fastness properties of the treated samples were not changed. In the case of light fastness properties, it was increased a little for 4% and 6% enzyme treated samples. Prog. Color Colorants Coat. 2(2009), 1-6. © Institute for Color Science and Technology.

1. Introduction

In recent years, the use of low-environmental impact biotechnology has given rises to new types of treatment in the textile industry [1]. The best-established application of biotechnology to textiles is the use of enzymes. These vital parts of all living organisms are organic catalysts, which specify the reaction catalysis and select the substrates. Some traditional chemical treatments can be replaced by enzyme treatments, because of their lower product quality, higher manufacturing cost, more waste and added energy consumption. The main enzymes used in textile processing are amylases, cellulases, proteases, esterases, nitrilases, catalases, peroxidases, laccases and pectin-degrading enzymes [2, 3].

A great many studies have been done on applications of proteases, including antifelting and antishrink finishings, oxidative treatments followed by proteolysis, pilling performances, surface and appearance modification of wool fibers [4, 5].

It has been demonstrated that the hydrophobic

*Corresponding author: mparvinzadeh@gmail.com

properties and scaly structure of the wool surface are the main factors causing shrinkage. Proteases have been used for descaling process to improve shrink resistance [4].

Some of enzymatic processes on wool fibers described that proteolytic enzyme will improves the pilling behavior, the handle and luster of wool fabrics [5].

There are relatively few papers study effects of protease on dyeing properties of wool with natural dyes and fruit wastes. Some researchers have reported the dyeing properties of two natural yellow pigments on the protease treated wool fibers. Protease enzyme also tends to improve natural dyes absorption on wool fibers [6, 7].

For several centuries, humans admired the beautiful natural colors of plants and minerals. Natural dyes have been known and used for thousands of years for body painting and coloring foods for ancient humans [8]. The greatest use of natural dyes occurred when the art of weaving developed [9-11]. Today dyeing processes based on natural sources have gained importance in view of stringent environmental and industrial safety conditions. Innovative ideas in natural dyeing of textiles are being tried to cater to such needs [12, 13]. Natural sources of dyes prepared for dyeing do not undergo any chemical operations. Those operations involved are purely physical, such as grinding, drying and water extractions. None of these operations created any great environment problems. Special color effects were also achieved in fibers dyed with natural dyes with good washing properties. The combination of natural sources with new processes could improve to expand into the added value of consumer goods [14].

Pistachio is a common name for a plant genus of the cashew family an evergreen shrub or small tree growing to 1 – 8 m tall with a long tradition in folk medicine since the ancients Greeks. It is one of the principal agriculture plants in Iran (the area under pistachio cultivation being about 430,000 acres) and the country is a major pistachio exporter worldwide (> 130; 000 tons for year 2002). The aerial part has traditionally been used as a stimulant, for its diuretic properties, and to treat hypertension, coughs, sore throats, eczema, tomach aches, kidney stones and jaundice [15].

Pistachio hulls contain phenolics as quercetin (14.9 microg/g), luteolin (10.0 microg/g), eriodictyol (10.2 microg/g), rutin (1.6 microg/g), naringenin (1.2 microg/g), apigenin (0.2 microg/g), and the anthocyanins, cyanidin-3-galactoside (696 microg/g) and cyanidin-3-glucoside (209 microg/g). The chemical composition of the essential oil also reveals the presence of several main compounds: myrcene (19-25%), a-pinene (16%), terpinen-4-ol (22%), d-3-carene (65%), limonene, b-pinene, a-phellandrene, sabinene, *para*-cymene and *g*-terpinene. The extracts of the phenolic compounds reveal considerable antimicrobial and antioxidant activity in particular antifungal activity [16, 17].

Waste materials from fruits generated during the food production process can be used directly in wool fiber dyeing with no necessary processing in advance. Commercial and institutional food producers can save money and protect the environment by introducing fruit wastes to dyeing sectors for producing added value products. Main centers that may benefit from this are restaurants, supermarkets, school cafeterias, hospitals, food processors, farmers, hotels, prisons, employee lunch rooms, parks and recreational facilities, and community events [18, 19]. In our previous studies on some fruit wastes such as onion, pomegranate and walnut shells, we produced bright shades on dyed wool yarns using ammonia treatment [20-22]. The present study is a new approach for using colorants extracted from pistachio hulls on wool fibers pretreated with protease enzymes.

2. Experimental

2.1. Materials and Methods

The wool was Iranian yarn of 432/2 Tex with 144 twists/meter. The nonionic detergent, used for scouring the wool, was obtained from Shirley Development Limited. The enzyme used was Novolan T from Novo Nordisk. It was produced by fermentation of genetically modified Bacillus microorganism. Acetic acid (85%) from Merck was applied for dyeing process. Powder of Iranian pistachio hulls was used for dyeing of protease treated wool yarns.

The Wool yarn was first scoured in 0.5% nonionic detergent for 30 mins. at 50ºC and a liquor ratio of 40:1. The enzym treatments were applied for 1 hr at pH 7 and 30ºC. Enzyme concentrations of 1, 2, 4 and 6% owf were used. The liquor ratio was 10:1. Following the enzymatic treatment, in order to denature the enzyme, the yarns were maintained for 5 mins. at a temperature of 90 ºC and a pH lower than 4,. Finally, the yarns were rinsed to eliminate any remaining enzyme. Dye solutions were prepared 24 hrs prior to dyeing by adding the pistachio hulls powder to water (50% owf, liquor ratio 50:1). The dyeing process was started at 40˚C and the temperature was raised to 85˚C over 20 mins. and then held at that temperature for 1 hr. The pH was maintained at 5 using acetic acid.

Some of physical, mechanical and colorimetric properties of the treated wool yarns (dyebath exhaustion, tensile strength, reflectance measurement, vertical wicking height and color fastness) were discussed. All measurements were repeated five times, together with standard deviation (the coefficient of variation was bellow 5% for all cases).

The effect of enzyme treatments on the percentage dyebath exhaustion was calculated according to Eq 1:

$$E= (A_{\circ}-A_d)/ A_{\circ} \times 100 \quad (1)$$

Where $A_{\circ}$ and A_d are the absorbances (at λ_{max}) of dye originally in the dyebath and of residual dye in the dyebath, respectively. The absorbances were measured, using a Shimadzu UV-2101 PC UV-Vis spectrophotometer.

The tensile strength of the enzyme treated and untreated wool yarns were evaluated using an Instron TE-500 from Farayab with gauge of 20 cm and a cross-head speed of 25 cm/min, after conditioning the specimen for 24 h and 65%, relative humidity and 20ºC (ASTM D2256).

The reflectance of the dyed samples was recorded using a GretagMacbeth COLOREYE 7000A spectro-photometer integrated with an IBM personal computer. CIELAB color coordinates (*L*, a*, b*, C** and *h*) were calculated from the reflectance data for 10º observer and illuminant D_{65}.

The effects of the enzyme solutions on the wicking properties of the yarns were also examined. For this purpose, samples were hung vertically in such a way that 1 cm of the sample soaked in the water container. After 1 min, the wet height of the samples was measured by means of a ruler. The samples were raw, scoured, and enzyme-treated (1, 2, 4 and 6%).

The wash-fastness properties of the samples were measured according to ISO 105-CO1. The color hue changes of the yarn and the degree of staining on the adjacent yarns were measured after drying. For light-fastness measurements, the yarns were exposed to the daylight for 2 and 7 days according to the daylight ISO 105-BO1, and the changes in the color (fading) were assessed by the blue scale.

3. Results and discussion

Table 1 shows the exhaustion values for the untreated and the enzyme treated wool yarns dyed with the pistachio hulls; The pistachio hulls shows much higher exhaustion on the sample treated with 1% enzyme solution than untreated samples. The increase in the enzyme concentration results from an increase in the dyebath exhaustion.

Table 1: Exhaustions of the untreated and enzyme treated wool yarns, dyed with pistachio hulls (Standard deviations in parentheses).

Enzyme (%)	Exhaustion (%)
0	55 (1.2)
1	73 (1.5)
2	74 (1.7)
4	77 (1.6)
6	85 (1.5)

Results of obtained from the vertical wicking tests on the enzyme treated wool yarns are shown in Table 2. It can be seen in Table 2 that the wicking height of raw wool increases with scouring; This means that the scouring process removes fiber fatty acids which are found in the cuticle surface. The enzyme treatment intensified the vertical wicking of the scoured wool.

Table 2: Vertical wicking height of the raw, scoured, and treated wool with 1, 2, 4 and 6% enzyme (CV was less than 5%).

Enzyme (%)	Wicking height (mm)
0 (Raw wool)	2
0 (Scoured wool)	7
1	9
2	10
4	13
6	15

Table 3 shows that the modulus, tenacity and extension at the breaking values for the sample treated with 1% enzyme were lower than those untreated. A greater decrease in the tenacity and extension at break can be seen by an increase in the enzyme concentration.

The *L**, *a**, *b**, *C** and *h* values of enzyme treated wool yarns dyed with the pistachio hulls and untreated, are given in Table 4. The lightness (*L**) values show decreases for the sample treated with 1% enzyme and further decreases as the enzyme concentration decreases. There are relatively small change in *a**, *b**, *C** and *h* for enzyme treated pistachio hulls dyed wool yarns.

The results obtained from the wash and light fastness tests are given in Tables 5 and 6. Enzymatic pretreatment does not affect the wash fastness for those samples dyed with the pistachio hulls.

After exposing the samples to daylight for 2 days, samples treated with 4 and 6% enzymes have indicated better light fastness than others.

With an extension of the duration of exposure to the daylight for 7 days, no more fading was observed. The color fading of the samples was limited to a certain period of the exposure to daylight.

Table 3: Tensile properties of untreated and enzyme treated wool yarns dyed with pistachio hulls (CV was less than 5%).

Enzyme (%)	Initial modulus (g/tex)	Extension at break (%)	Tenacity (g/tex)
0	28.3 (0.5)	31.5 (1.1)	6.23 (0.2)
1	25.1 (0.5)	28.4 (1.0)	5.42 (0.2)
2	23.8 (0.8)	27.5 (0.9)	4.83 (0.1)
4	22.9 (0.1)	25.08 (0.9)	4.81 (0.2)
6	20.4 (0.9)	22.04 (0.7)	3.77 (0.1)

Table 4: Color co-ordinates of the untreated and enzyme treated wool yarns dyed with the pistachio hulls (Standard deviations in parentheses).

Enzyme (%)	L^*	a^*	b^*	C^*	h
0	68.15 (1.2)	0.98 (1.0)	30.07 (1.1)	28.02 (1.0)	97.32 (1.8)
1	60.88 (0.7)	1.56 (0.5)	29.88 (1.0)	29.77 (0.9)	96.50 (1.5)
2	55.55 (0.2)	1.69 (0.6)	31.13 (0.3)	29.06 (0.7)	96.20 (2.1)
4	53.07 (0.4)	1.05 (0.1)	31.02 (0.8)	29.50 (0.8)	96.39 (0.4)
6	51.23 (0.9)	1.35 (0.8)	32.93 (0.4)	28.00 (0.5)	97.06 (0.7)

Table 5: Wash fastness properties of untreated and enzyme treated wool yarns dyed with pistachio hulls

Enzyme (%)	Wash fastness	Staining on wool	Staining On cotton
0	4	4	4
1	4	4	4
2	4	4	4
4	4	4	4
6	4	4	4

Table 6: Light fastness properties of the untreated and enzyme treated wool yarns dyed with the pistachio hulls.

Enzyme (%)	After 2 days	After 7 days
0	3-4	3-4
1	3-4	3-4
2	3-4	3-4
4	4	4
6	4	4

Wool yarns were treated with 1, 2, 4 and 6% protease solutions for 1 hr. Results of the UV–Vis spectrophotometry analysis on the remaining dyebath solutions showed that enzyme increased absorption of the pistachio hulls extracts into the fiber.

Wool, a complex natural fiber composed mainly of proteins (97%) and lipids (1%), is an ideal substrate for protease enzyme. It consists of two major morphological parts of the cuticle and the cortex. Cuticle is the barrier for dye and penetration, due to the highly crosslinked structure by the large amount of disulphide and the bound lipid materials. When wool is used as a substrate for enzyme treatment, at the first step, enzyme is absorbed at the fiber surface. Then it is diffused through the fiber surface into the fiber bulk and finally it catalyzes reactions in the fiber. Protease catalyzes the degradation of epicuticle, and as a consequence, it improves the susceptibility of dyes attraction. On the other hand, the effect of increased dye absorption is mostly due to the damage at the cuticles edge, progressive damage to the matrix proteins and macrofibrils in the fiber cortex, which are allowing the dye molecules to penetrate more easily into the fiber cortex. The vertical wicking height is also intensified by the enzyme treatment (2, 4, 5, 7). Further degradation is shown with the increase in the enzyme concentration. The ncrease in wicking height confirms that the protease catalyse rate is increased with any increase in the enzyme concentration. Cuticle provides a hydrophobic barrier at the fiber surface while the protease hydrolyses cuticle improve moisture diffusion from the surface into the fiber. These results are in agreement with the results obtained from the dyebath exhaustions. It can be seen for the results of tensile strength, enzyme penetrates into the fiber resulting degradation the cortical cells. Increase in enzyme concentration caused more degradation and structural damage [13].

The color measurement tests confirmed that L^* values decreased with the treatment of enzyme, and also that any increase in the percentage of enzyme in the solution caused a decrease in the amounts of L^*. There was no considerable change in wash-fastness test for enzyme treated and pistachio hulls dyed wool yarns. In the case of light fastness properties, it was increased for samples treated with 4 and 6% enzymes.

Many factors influence the light fastness of dyes, including the chemical and physical state of the dye within the fiber, the fiber substrate, dye concentration in the fiber, dye environmental factors, the source and intensity of illumination, and the presence of UV absorbers and other additives in the dyebath. The decrement of dye concentration is a function of the irradiation time. On the other hand, the light fastness increases with the increase of dye concentration in a fiber. In general, the dissipation of absorbed energy of light is easier when more dye is absorbed by the fiber, and consequently the photo-degradation process is slower (24, 25). The enzyme treatment causes the dye diffusion into the fiber to increase and shades become darker. As a result, the absorbed dyes are less vulnerable to the effects of light. Protease hydrolyses hydrophobic barrier on the fiber surface improve the dye absorption into the fiber.

4. Conclusions

Wool yarns were treated with 1, 2, 4 and 6% protease solutions for 1 h. Results of the UV-Vis spectrophotometry analysis on the remaining dyebath solutions showed that enzyme increased absorption of the pistachio hulls colorants into the fiber. These results are similar to the results obtained from vertical wicking test. The color measurement tests confirmed that L^* values decreased with the treatment of enzyme, and also that any increase in the percentage of enzyme in the solution caused an increase in the amounts of $L*$. There was no considerable change in washfastness test for enzyme treated pistachio hulls dyed wool yarns. In the case of light fastness properties, it was increased for samples treated with 4 and 6% enzymes. Scouring process disrupts hydrophobic barrier at the fiber surface where it allows the proteases to reach the protein layers of the wool cuticle as a whole. Protease damages the cuticle's edge and overlapping area and to progressive damage to the matrix proteins and to the macrofibrils in the fiber cortex, allowing the dye molecules to penetrate more easily into the fiber cortex.

5. References

1. Y. M. Galante, D. Foglietti, C. Tonin, R. Innocenti, F. Ferrero, R. Monteverdi, Enzyme applications in fiber processing, Symposium on Enzyme Applications in Fiber Processing. *Am. Chem. Soc.* 24(1998), 294-305.
2. N. Duran, M. Duran, Enzyme applications in the textile industry. *Rev. Prog. Color.* 30(2000), 41-44.
3. A. Cavaco-Paulo, G. M. Gubitz, Textile processing with enzymes, Woodhead Publishing Limited, USA, (2003), 180.
4. D. P. Bishop, J. Shen, E. Heine, B. Hollfelder, The use of proteolytic enzymes to reduce wool fiber stiffness and prickle. *J. Tex. Inst.* 89(1998), 546-553.
5. G. Mazzucheti, C. Vineis, Study of the enzyme treatments effect on the pilling behavior of knitted wool fabrics. *Aut. Res. J.* 5(2005), 55-60.
6. E. Tsatsaroni, K. M. Liakopoulou, I. Eleftheriadis, Comparative study of dyeing properties of two yellow natural pigments: Effects of enzymes and proteins, *Dyes Pigments*. 37(1998), 307-315.
7. M. Parvinzadeh, Effect of proteolytic enzyme on dyeing of wool with madder. *Enzym. Micro. Tech.* 40(2007), 1719-1722.
8. Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley Ltd, Canada, 25(1998), 650-675.
9. A. U. Pope, and P. Ackerman, A survey of Persian Art, Soroush Press, USA, (1977), 230-237.
10. R. Anavian, G. Anavian, Royal Persian & Kashmir Brocades, Senshoku to Seikatsusha Ltd, Japan, (1975), 25-75.
11. I. Holme, Unrevealing nature's mysteries, *Int. Dyer Text. Printer*. 173(1988), 8 and 26.
12. U. Sewecow, Present day significance of natural dyestuffs in textile dyeing, *Melliand Textileber*. 5(1995), 89-92.
13. C. E. Pellew, Dyes and Dyeing, Abhishek Publications, India, (1998), 80-89.
14. W. S. Murphy, Encyclopedia of Textile Technology, Abhishek Publications, India, (1999), 50-55.
15. S. Abbasi, F. Vahabzadeh, M. Mehranian, Profiles of phenolics and antioxidant activity of pistachio hulls during solid-state fermentation by phanerochaete chrysosporium-involvement of lignin peroxidase and manganese peroxidase. *Scientia Iranica*. 14(2007), 373-378.
16. N. P. Seeram, Y. Zhang, S. M. Henning, R. Lee, Y. Niu, G. Lin, D. Heber, Pistachio skin phenolics are destroyed by bleaching resulting in reduced antioxidative capacities. *J. Agric. Food Chem.* 54(2006), 7036-7040.
17. N. Benhammou, F. A. Bekkara, T. K. Panovska, Antioxidant and antimicrobial activities of the Pistacia lentiscus and Pistacia atlantica extracts. *African J. Pharmacy Pharmacology.* 2(2008), 22-28.
18. M. Doble, A. Kumar, Biotreatment of Industrial Effluents. Butterworth-Heinemann Publisher, Germany, (2005), 55.
19. M. Fehr, M. D. R. Calcado, C. D. Romao, The Basis of a Policy for Minimizing and Recycling Food Waste. *Environ. Sci. Pol.* 5(2002), 247-253.
20. M. Montazer, M. Parvinzadeh, A. Kiumarsi, Colorimetric properties of wool dyed with natural dyes after treatment with ammonia. *Color. Technol.* 120(2004), 161-166.
21. M. Montazer, M. Parvinzadeh, Effect of ammonia on madder-dyed natural protein fiber. *J. Appl. Polym. Sci.* 93(2004), 2704-2710.
22. M. Montazer, M. Parvinzadeh, Dyeing of Wool with Marigold and Its Properties. *Fibers Polym*. 8(2007), 181-185.
23. H. Nolte, D. P. Bishop, H. Hocker, Effects of proteolytic and lipolytic enzymes on untreated and shrink-resist-tested wool. *J. Tex. Inst.* 87(1996), 212-226
24. J. Oakes, Photofading of textile dyes. *Rev. Prog. Color.* 31(2001), 21-28.
25. A. T. Balazsy, D. Eastop, Chemical principles of textile conservation, John Wiley ltd, Singapore, (1998), 36-41.