Antibacterial Dyeing of Wool with Natural Cationic Dye Using Metal Mordants

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crossref http://dx.doi.org/10.5755/j01.ms.18.3.2437

Received 28 February 2011; accepted 10 November 2011

In this study, Berberine colorant extracted from *berberis vulgaris* root was applied on wool fiber using alum (aluminum potassium sulfate), copper sulfate and potassium dichromate as mordant. The effect of treatment variables such as amount of mordant, time and temperature on the color strength of dyed fibers was examined. The fastness properties of dyed wool against washing, light and wet rubbing were evaluated. the use of metal mordants increased the color strength of the dyed goods. Increase in dyeing time and temperature caused deeper shades. All mordants, increased the rub fastness and wash fastness of dyed samples, but the light fastness was increased except in case of alum. Berberine is a cationic dye and because of it's quaternary ammonium structure can act as an antibacterial agent. So, dyed samples were tested for antibacterial activity using AATCC test method 100-2004. The dyed wool represented a high level of antibacterial activity. The extract of the *berberis vulgaris* can be considered as a natural dye of acceptable fastness properties together with excellent antibacterial activity for woolen textiles.

Keywords: wool, berberine, antibacterial, dyeing, natural dye.

1. INTRODUCTION

Natural dyes and pigments are found in some plants, animals, insects, bacteria, fungi and minerals. For example alizarin is a very old and common red dye found in roots of madder, *rubia tinctoria*. Development of synthetic dyes in the last century, reduced the use of natural dyes in modern dyeing [1 – 3]. Synthetic dyes are produced from cheap petroleum sources, and generally have easy dyeing with superior fastness properties. But there are drawbacks about synthetic dyes mainly toxicity and environmental pollution caused by waste water expelled from dye-houses.

Recently, a new tendency to natural dyes has raised mainly due to their environmentally friendly characteristics [1, 2]. They are considered to give several advantages to several applications such as non toxic functions, specific medical actions and environmentally friendly finishes [2]. Natural dyes are clinically safer than their synthetic analogs in handling and use because of non carcinogenic and biodegradable nature [3 – 5]. Another factor driving interest in natural dyeing can be attributed to strict regulations and laws enacted by governments in response to consumer concerns [6].

Microbes are the tiniest creatures not seen by the naked eye. They include a variety of micro-organisms like Bacteria, Fungi, Algae and viruses. Bacteria are unicellular organisms which grow very rapidly under warmth and moisture. Sub divisions in the bacteria family are Gram positive (Staphylococcus aureus), Gram negative (E-Coli), spore bearing or non spore bearing type. The growth of microbes on textiles during use and storage negatively affects the wearer as well as the textile itself. The detrimental effects can be controlled by durable antimicrobial finishing of the textile using broad-spectrum biocides or by incorporating the biocide into synthetic fibers during extrusion. Some active antimicrobial agents used for antimicrobial finishing of textiles are silver, quaternary ammonium salts, polyhexamethylene biguanide, triclosan, chitosan, dyes and regenerable *N*-halamine compounds and peroxyacids [7, 8]. Furthermore, some natural dyes, when applied on textiles, show antibacterial effects, so can be considered as functional dyes with health care properties. Lawsone, a natural dye extracted from henna, when applied on wool fabric, has shown antibacterial effect [7]. In other researches [2, 8] cotton and nylon fabrics dyed with natural colorant extracted from Amur cork tree, has shown antibacterial activity. *Rhizoma coptidis* extract has been applied on wool fiber and antibacterial property has been observed [1].

Berberis Vulgaris is a shrub, which is extensively implanted in southern khorassan-Iran and many other places all over the world, for its valuable fruit, barberry.

In this study, the roots of this plant, have been used as a source of a natural colorant. There is a natural yellow dye in these roots named Berberine [9]. The amount of the dye is less in the woods of the plant. This natural cationic dye was extracted and applied on wool fiber. Three mineral compounds namely alum (aluminum potassium sulfate), copper sulfate and potassium dichromate were applied onto wool as mordant prior to dyeing. The effect of mordanting on the dye strength and fastness properties was studied. Finally the antibacterial property of dyed fibers was tested according to AATCC 100-2004.

2. EXPERIMENTAL

2.1. Materials

Woolen yarn (Nm = 400, 2 ply) was purchased from local wool spinning mill. To remove any natural or synthetic impurities, the yarns were scoured using 2 g/l non-ionic surfactant (Ultravon CN, Ciba) and 2 ml/l ammonia at 45 °C for 30 minutes (L : G = 30 : 1) and then rinsed and air dried. L : G represents the liqour to goods ratio.

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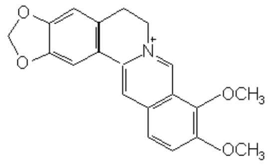

Fig. 1. Chemical structure of Berberine [10]

Berberis Vulgaris roots were first washed and dried and then chopped and powdered. To prepare the original solution of the dye, each 100 g of powder was added to 1 L of distilled water and boiled for 2 hours and then filtered. The concentration of the resultant solution is 10 % W/V. Acetic acid and ammonia were analytical grade reagents from Merck.

2.2. Methods

Mordanting. The scoured wool yarns were mordanted using different amounts (1, 2, and 5 % owf) of alum, copper sulfate and potassium dichromate mordants at 80 °C and L : G = 30 : 1, for 45 minutes. Generally, mordanting was done prior to dyeing. After mordanting the each sample was rinsed with 100 ml of distilled water.

Dyeing. 100 ml of original dye solution was mixed with 100 ml of distilled water for each 5 gram of wool (L : G = 40 : 1). The pH of the dyebath was adjusted on 5 using acetic acid . The dyeing was started at 40 °C and the temperature was raised to final temperature (60, 70, 80, 90 °C) at the rate of 2 °C per minute. Then the samples remained in that condition for appropriate time (45, 60, 90 minute), and then rinsed and air dried. All mordanting and dyeing processes were carried out using a laboratory dyeing machine made by Rissanj co.-Iran.

Color measurements. The reflectance of dyed yarns and color coordinates CIE *L**, *a**, *b** values were measured on a Color-eye 7000A spectrophotometer using illuminant D65 and 10° standard observer. For each sample, three measurments on three different places were made and the average values were reported. Color strength (*K*/*S*) of dyed samples was calculated using Kubelka-Munk equation:

$$K/S = (1 - R)^2 / 2R, \quad (1)$$

where *R* is the observed reflectance, *K* is the absorption coefficient and *S* is the light scattering coefficient.

Color fastness tests. Color fastness to washing (rating 1 for low and 5 for high fastness), light (rating 1 for low and 8 for high fastness) and rubbing (rating 1 for low and 5 for high fastness) was measured according to: ISO 105-C01: 1989(E), ISO 105-B02: 1994(E), ISO 105-X12: 1993(E) respectively.

Antibacterial test. The antibacterial property of dyed yarns was quantitatively evaluated according to AATCC 100-2004. The bacterial species used were: *Klebsiella pneumoniae* (Gram negative) and *Staphylococcus aureus* (Gram positive). The colonies of both bacteria before and after incubation on the agar plate were counted by microscope. The reduction in the number of bacteria, which was calculated using equation (2), shows the efficacy of the antibacterial treatment.

$$E = [(N_1 - N_2)/N_1] \times 100 \ [\%], \quad (2)$$

where N_1 is the number of bacteria colonies at the beginning of the test (0 hour), and N_2 is the number of bacteria colonies after 24 hours contact of dyed yarns [8, 10, 11].

3. RESULTS AND DISCUSSION

3.1. Effect of mordants

Figure 2 shows the effect of amount of three mordants on the color strength of dyed samples. The increase in K/S and decrease in *L** (Tables 1 and 2) of samples shows that increasing of the amount of mordants from 0 % owf to 5 % owf caused more absorption of the dye to the fibers and deeper shades.

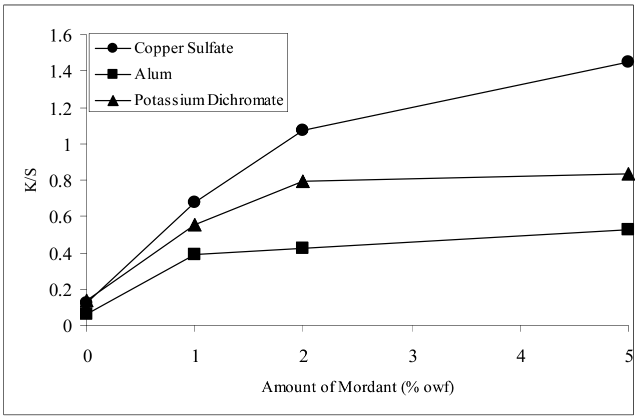

Fig. 2. The effect of amount of three mordants on the color strength of pre-mordanted and dyed samples (60 min, 80 °C)

Table 1. Color coordinates of scoured raw wool and scoured samples mordanted with 2 % of each mordant

Mordant	*L**	*a**	*b**
–	85.56	–0.44	14.34
Alum	82.02	–0.12	10.22
Copper sulfate	69.57	–6.67	14.80
Potassium dichromate	73.14	3.21	19.01

Table 2. Color coordinates of samples dyed (60 min, 80 °C) after mordanting with different amounts of mordants

Mordant	% owf	*L**	*a**	*b**
Copper sulfate	1	62.05	–0.20	40.77
Copper sulfate	2	55.59	–2.22	35.72
Copper sulfate	5	51.29	–2.25	30.35
Alum	1	71.15	0.21	49.01
Alum	2	70.39	1.17	47.60
Alum	5	69.73	1.01	47.32
Potassium dichromate	1	67.05	1.48	46.34
Potassium dichromate	2	62.69	3.19	42.28
Potassium dichromate	5	61.77	2.5	42.32

The metal ions can form coordinate complexes with amino groups of wool fiber. Some co-ordination sites remained un-occupied when they interacted with the fibre and can form complexes with dye molecules. These metals formed a binary complex with the fibre with dye. Such a strong coordination tendency enhanced the interaction between the fibre and the dye, resulting in the high dye uptake [12].

It is obvious from Figure 2 that copper sulfate has the greatest effect on dye absorption when the amount of mordant increased from 1 % owf to 5 % owf. In the case of alum and potassium dichromate mordants, the increase of color strength when the amount of mordant increased from 1 % owf to 2 % owf is greater than when increased from 2 % owf to 5 % owf. So because of the little effect of increasing of mordant from 2 % owf to 5 % owf and to prevent from damaging effect of mordants on fiber strength, 2 % owf is considered as the optimum amount of mordants.

3.2. Effect of dyeing time

Figure 3 shows the effect of time on the color strength of dyed samples pre-mordanted with three mordants. The color strength increased with increasing the dyeing time. In the case of Copper sulfate the time has the most increasing effect and for alum, it has the less increasing effect on dye exhaustion. Also the color strength increased when the dyeing time increased from 30 minutes to 75 minutes, after which the increase in time had no significant effect on dye absorption. It should be due to this fact that, the dye molecules present in the fiber and the dyebath has reached to equilibrium after 75 minutes.

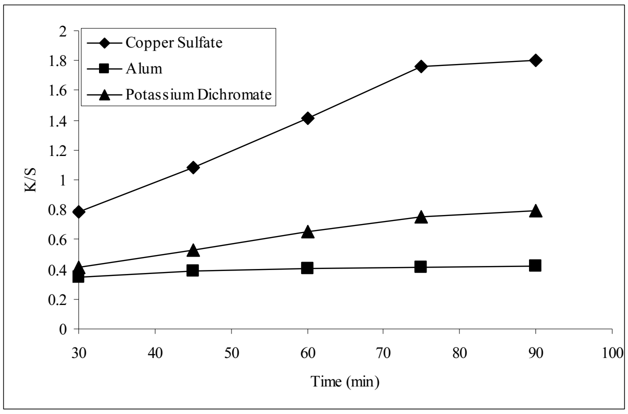

Fig. 3. The effect of time on the color strength of dyed samples (80 °C) pre-mordanted with three mordants

3.3. Effect of dyeing temperature

Figure 4 shows that increase in dyeing temperature from 60 °C to 90 °C leads to increase in color strength for all mordants. The most effect is observed in the case of copper sulfate mordant. As the temperature raised, the wool fiber swelling and the breakdown of dye molecule aggregates in the solution became more, thus the diffusion of the dye molecules to the fiber became easier and thus the exhaustion and *K*/*S* increased [11, 13, 14].

3.4. Fastness properties

Table 3 shows the fastness properties of mordanted and non-mordanted dyed wool. All fastness properties of dyed samples when mordanted are higher than when non-mordanted . This increase is due to increase in size of dye molecules when connected to metal atoms into the fiber [14]. Wet rub fastness was less than dry rub fastness because the water molecules can dissolve some of water-soluble dye molecules and make them easier to be removed from the fiber by rubbing. All fastness properties of mordanted and then dyed wool fibers are generally acceptable.

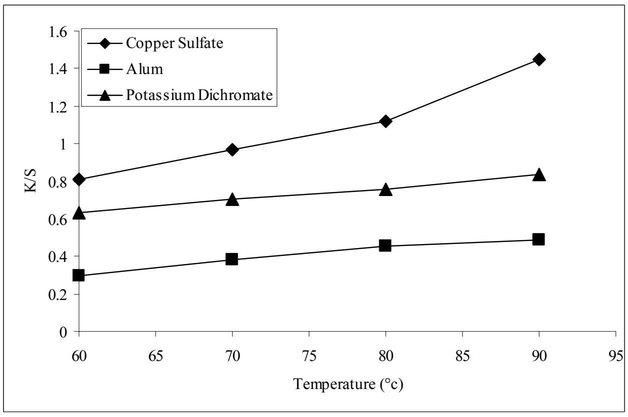

Fig. 4. The effect of dyeing temperature on the color strength of dyed samples (60 min) pre-mordanted with three mordants

3.5. Antibacterial activity

Table 4 shows the percent reduction in number of two bacteria after 24 hours incubation on the surface of undyed, mordanted and dyed (after mordanting with 2 % owf of all mordants) wool. It is obvious that with all mordants, the dyed wool has excellent antibacterial activity against both bacteria used in this study. Samples mordanted with copper sulfate, potassium dichromate and alum show only a low antibacterial activity. It means that the most antibacterial activity is because of the presence of berberine colorant in the mordanted and dyed samples. This finding is in agreement with the results of references [1, 11, 13]. As shown in Figure 1, the berberine colorant, is a quaternary ammonium compound, containing a positive charge on N atom that could destroy the negatively charged cell membrane of the bacteria by disturbing charge balances of cell membrane. Other detrimental effects of quaternary ammonium compounds on microbes, are denaturizing of proteins and disruption of the cell structure [1, 8, 10, 15, 16]. During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antimicrobial ability as long as the compound is attached to textiles [8].

Table 3. Fastness properties of dyed samples (60 min, 80 °C) (pre-mordanted with 2 % owf of mordants)

Mordant	Wash Fastness	Rub Fastness (dry)	Rub Fastness (wet)	Light Fastness
Copper sulfate	4 – 5	4 – 5	3	6
Alum	5	4 – 5	3 – 4	5 – 6
Potassium dichromate	4	4 – 5	3 – 4	6 – 7
Without Mordant	3 – 4	4	2 – 3	5 – 6

4. CONCLUSIONS

Beberine which is a cationic colorant present in the extract of *berberis vulgaris* root can be used as a natural dye for wool. Mordanting with copper sulfate, alum and Potassium dichromate before dyeing increased the dye uptake and fastness properties of the samples. Only in case of alum mordant, light fastness was not increased. Wool fiber dyed with this dye has great antibacterial activity against both gram positive and gram negative bacteria. Furthermore because only 2 % of the mordant is sufficient for this dyeing process which is low compared with mordant dyeing and conventional natural dyeings and a high amount of the used mordant is absorbed by the wool fibers, the amount of mordants repelled by the waste water is very low and the process can be considered as environmentally friendly and has the minimum pollution. This natural dye can be used for dyeing wool with good fastness and excellent antibacterial properties.

Table 4. Antibacterial activity of different samples (mordanted with 2 % owf of mordanr, dyed at 80 °C for 60 min) (% reduction of bacteria after 24 hr incubation)

Sample	Bacteria	
	Staphylococcus aureus	*Klebsiella pneumoniae*
Control (undyed)	0	0
Unmordanted – dyed	30.1	31.3
Copper sulfate mordanted	15.1	14.9
Copper sulfate mordanted – dyed	99.5	99.6
Alum mordanted	7.3	6.9
Alum mordanted – dyed	99.4	99.5
Potassium dichromate mordanted	6.4	6.5
Potassium dichromate mordanted – dyed	99.6	99.5

Acknowledgments

The author gratefully acknowledges the help and support of Dr. Ebrahim Haji for performing antibacterial tests.

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