The Study of Punica granatum Absorption Behavior on wool fibers by using Spectrophotometric Data

A. Shams-Nateri

Textile Engineering Dep., Guilan University, Rasht, Iran

Abstract

In This work, the absorption behavior of Punica granatum or Anar as Iranian natural dye on wool fibers was studied by using spectrophotometer data of dye solution. Initially, wool yarn were scoured and mordanted with Alum. Then wool yarn was dyed with anaar as an Iranian natural dyes. In next stage, the wastewater of dye bath was reused for wool dyeing. For spectrophotometry study, the absorbance spectral of dye solution was measured by spectrophotometer. Then, the absorbance values of dye solution were used to determine dye concentrations in the wastewater of dyebath and absorption by wool fibers. The result indicated that the exhaustion and shade of dye solution changed by variation in Alum concentration. The hue of wastewater differs from initial dyebath.

Keywords: Natural dye, Anar, Punica granatum, Wool, Dyeing, Mordant, Spectrophotometer.

1. Introduction

Recently, a revival interest in the use of natural dyes in textile coloration has been growing. This is a result of the stringent environmental standards imposed by many countries in a response to the toxic and allergic reactions associated with synthetic dyes. Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than their synthetic counter parts. Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment. Considerable research work is being undertaken around the world on the application of natural dyes. Many plants have a natural dye potential in their leaves, stems, flowerheads, berries, etc. from very early times, As long as 5000 years ago, madder and indigo were in used in many parts of the world. Considerably later, the discovery of the Americas led to the wider use of the other great natural dyes such as logwood, fustic and cochineal. Natural dyestuffs fall mainly into the following broad categoris: leaves and stems; twigs and tree pruning; flower heads; barks; roots; insect dyes; outer skins; hulls and husks; heartwoods and wood-havings; berries and seeds; and lichens[1-7].

Since prehistoric times, natural dyes have been used for many purposes such as the coloring of natural fibers wool, cotton and silk as well as fur and leather. The dyes were also used to color cosmetic products and to produce inks, watercolors and artist's paints. The use of natural dyes to color textiles declined rapidly after the discovery of synthetic dyes in 1856, until they were virtually unused by 1900. Most natural dyes have poor to moderate light fastness, while synthetic dyes represent the full range of light fastness properties from poor to excellent. The analysis of the natural dyes listed in Color Index revealed that almost 50% of all natural dyes used to color textiles are flavonoid compounds. Most of the remaining natural dyes fall within three chemical classes anthraquinones, naphtoquinones and indigoids. Although flavonoid compounds are not very light fast, anthraquinones and indigoids are noted for their excellent light fastness. However, the light fastness of anthraquinones is decreased as the number of hydroxyl substituent groups is increased. Other aspects of chemical structure may affect the light fastness, such as the symmetry of the dye molecules: symmetrical dye molecules usually exhibit greater light fastness than non-symmetrical dye molecules, and larger dye molecules generally provide faster dyeing than smaller ones[1-7].

The word 'mordant' comes from the latin morder meaning 'to bite' as in 'to fasten on to'. Mordanting is the process of pre-treatment of fibers, which allows the applied dye color to be permanently fixed. The type of mordant used will affect the color produced by the dyestuff, so a variety of shades can be produced from a single dyebath by treating individual skeins of yarn with different mordant. The mordant used with natural dyes include chromium, aluminum, iron, cupper, tin and other heavy metal and polluting salts. Aluminum commonly called alum. Alum is a white powder that is safe to had and easy to use. Alum produces bright shades and gives relatively good light-fastness. If used in excess, alum will make wool feel sticky, so it is recommended that you measure accurately. Cupper has been used as cupper sulfate, a beautiful blue color when dissolved in water. Cupper darkens colors and gives a greenish cast. It provides good color-fastness and is not as hard on fibers as iron. A solid cupper pot will make an excellent cupper mordant [1-7].

Spectrophotometry: An absorption spectrum (a plot of A vs. λ) is used to show what wavelengths of light are absorbed by a sample. The peaks in the spectrum correspond to wavelengths that are strongly absorbed. These peaks are often referred to as "absorption maxima" and the wavelength at which these peaks occur are called λmax's. We can use λ max values to predict what color the sample may look like. When white light (containing all the visible wavelengths) is shined on a sample. Those colors corresponding to λ max's will be absorbed while the others pass through. The complementary color to the λ max will usually be the color that dominates and will therefore determine what color the sample appears. The absorption spectrum and λ max values can be used to help identify a substance, but are usually used to

determine the amount of a known substance in a sample. This is done using Beer's Law and a calibration curve [9-14].

Under many circumstances, the absorbance of a solution at a particular wavelength of light is directly proportional to the concentration of the substance in solution. This is the Beer-Lambert Law (often just called Beer's Law) and is written as:

$$A = Log(\frac{I_0}{I}) = \varepsilon \times L \times C \qquad (1)$$

Where A= absorbance

ε = absorptivity (a constant for a substance at a given wavelength)

L = path length (the distance the light travels through the sample)

C = concentration

Typically, molarity is used for concentration, cm for path length and liter mole-1 cm-1 for absorptivity. Absorbance has no units, and the proportionality constants inherent in both the Beer and Lambert observations are combined into one factor known as the extinction coefficient, ε. An extinction coefficient is constant at a given wavelength for a given solute that absorbs light. Since absorbance values are unitless, the extinction coefficient is most often expressed in units of inverse concentration times inverse path length (i.e., $M^{-1}cm^{-1}$, $mM^{-1}cm^{-1}$, $(mg/ml)^{-1}cm^{-1}$).

Beer's law showed us that, at a given wavelength, the absorbance is proportional to the concentration of the absorbing compound in solution. This fact can be used to create a calibration curve. A calibration curve is prepared by plotting the absorbance of a series of standards (solutions of known concentration) at a particular wavelength (usually at a λ max) as a function of their concentration (use any units you choose as long as they are consistent). The result will be a straight line. If the unknown sample's absorbance is also measured, its concentration can be determined from the calibration curve.

In general, it is possible to determine the concentration of a colored species in a given solution by measuring the absorbance of the solution at a certain specific wavelength and comparing the value obtained with a calibration curve obtained at the same wavelength[8-14].

2. Material and Methods:

The Iranian wool yarn of 10/2 metric, the nonionic detergent, Acetic acid, potash Alum, Anar (an Irannian natural dye), pH meter, Cintra10 UV-Visible pectrophotometer.

Woolen yarn dyed with Anar in bottom mordant methods as follow:
1. Scouring: The woolen yarn was scoured in 2 gr/lit anionic detergent, at liquor ratio 20:1, for 15 minuet at 70 ^{o}C.
2. Mordanting: wool yarn was mordanted by 1.25,2.5,3.75,5 gr/lit potash Alum at liquor ratio 40:1, with pH=4 (adjusted by acetic acid). Initial temperature was 40 ^{o}C. The temperature raised to boiling over 20 minute and continue at the boil for 60 minute. At the end, yarn was scoured by water and dried in environments.
3. Preparing the dyeing bath: The natural dye was dissolved in pure water. Then temperature raised to boiling point and continued at the boil for 60 minuet. Then the temperature was decrease to environment temperature and continued at this temperature for 24 hr.
4. Calibration dye solution: At first, series of known concentrations solutions was prepared and their absorbance was measured by spectrophotometer. Establish the λmax of

sample or find wavelength at which the substance has the largest absorbance (lowest %transmittance). The Absorbance at this wavelength will be most sensitive to concentration of dye. Plot dye concentration on the y-axis as a function of absorbance (A) at λmax on the x-axis and determine the linear relationship between concentration and absorbance at λmax . Then, the concentration of unknown dye solution (such as exhausted dye solution or waste water) by using the equation of this line and absorbance at λmax.
5. Dyeing (first step): mordanted yarn was dyed with 7.5, 10, 15 gr/lit Anaar at liquor ratio 40:1, with pH=4 (adjusted by acetic acid). Initial temperature was 40 ^{o}C. The bath temperature raised to boiling over 20 minute and continued at the boil for 60 minute. The absorbance spectral of wastewater was measured by spectrophotometer. The absorbance spectral of wastewater was measured by spectrophotometer and the concentration exhausted dye solution or waste water was calculated by absorbance at λmax . Absorpted dye by wool fiber was calculated by following Equation:

$$C_F = C_0 - C_S \qquad (2)$$

Where C_0 is dye concentration at dyebath, C_S is dye concentration at exhausted dyebath and C_F is dye concentration, which absorbed by wool fibers.

6. Dyeing by wastewater (second step): After removing the wool yarns from dyebath, the exhausted dye solution was reused for wool dying. At first, pH and liquor ratio of dyebath was adjusted. Initial temperature of dyeing dyebath was 40 ^{o}C. The temperature raised to boiling over 20 minute, And continues at the boil for 60 minute. The absorbance spectral of wastewater was measured by spectrophotometer. The dye concentration of exhausted dye solution or wastewater was calculated by absorbance at λmax. Dye absorption by wool fiber was calculated by Equation 2.

3. Results and Discussion:

The absorbance spectral of initial dye solution and the wastewater of dye bath in first and second stage are shown in figures 1. From these figures, The absorbance of initial dye solution differ over exhausted dayebath solution.
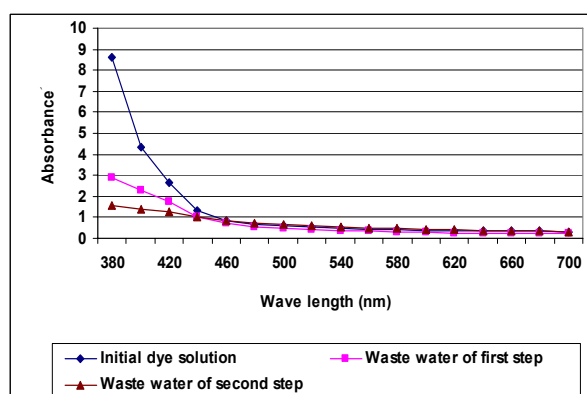

Figure 1. Absorbance spectral of dye solution (15 gr/lit dye dye and 5 gr/lit Alum)

The Location of initial dye and wastewater of first and second dyeing are shown in figures 4, 5 and 6 in CIELAB color space for D_{65} illuminant and 10° standard observer. The results indicate that the lightness (L*) increase by reusing dye solution. The chroma

(C*) of dye solution are decreased by reusing the dyebath. The hue angles of dye solution change less than the lightness (L*) and chroma (C*).
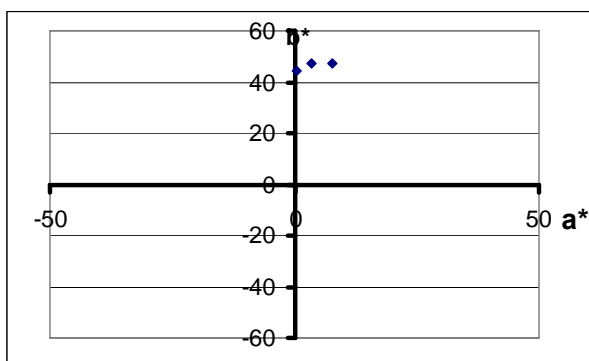

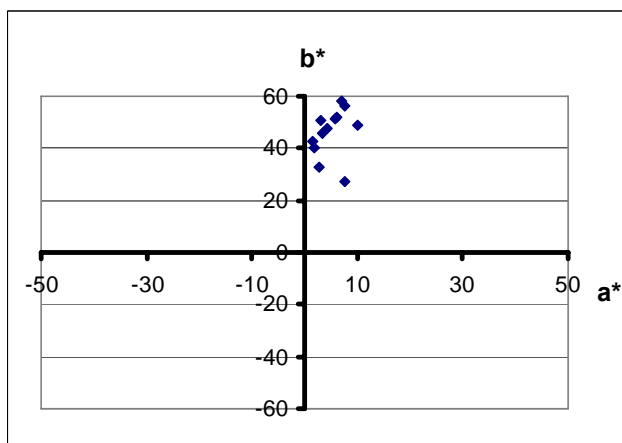Figure 2. Location of initial dye solution in CIELAB color space

Figure 3. Location of wastewater solution of first step dyeing in CIELAB color space
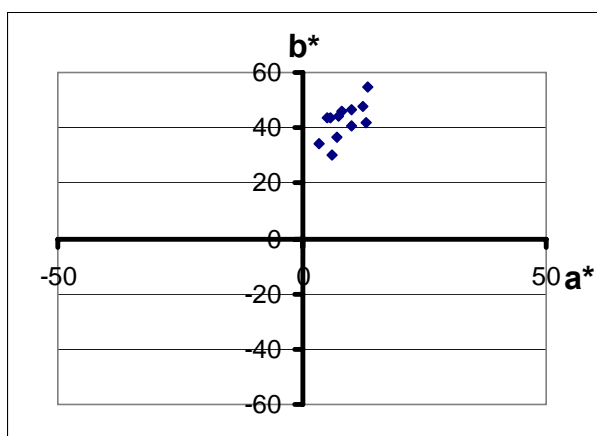

Figure 4. Location of wastewater solution of second step dyeing in CIELAB color space

In next stage, the absorbance spectra data was used to predict dyes concentration in initial and exhausted dyebath. The dye absorption on wool fiber was calculated by equation 4 from dye concentration in initial dye solution and wastewater. The result are summarized in Table 1. As observed from Tables 1, the dye exhaustion in second stage (wool dyeing by exhausted dyebath) are poor than first stage. The dye exhaustion is a function of the mordant concentration.

Table 1. Dyeability of anar on wool yarn

No.	Dyeing stage	Dye concentration (gr/lit)	Alum Concentration (gr/lit)			
			1.25	2.5	3.75	5
1	first	7.5	5.30	4.244	5.45	5.39
2	first	10	7.2	5.782	4.08	6.29
3	first	15	10.27	7.699	10.26	11.37
4	second	7.5	0.6	1.242	0.66	1.25
5	second	10	0.92	1.224	3.64	1.40
6	second	15	0.73	3.760	1.72	2.22

4. Conclusion:

In This work, the absorption behavior of anar as an Iranian natural dye on wool fibers was studied by using spectrophotometeric data. Initially, wool yarn were scoured and mordanted with potash alum. Then, wool yarn was dyed with anar dye. In next stage, the wastewater of dye bath was reused for wool dyeing. For spectrophotometry study, the absorbance spectral of dye solution was measured by spectrophotometer. Then, the absorbance values of dye solution were used to determine dye concentrations in the wastewater and absorption by wool fibers.

The result indicated that the exhaustion and shade of dye solution was changed by variation in alum concentration. In addition, the hue of wastewater differs over initial dyebath. The Location of initial dye and wastewater of first and second dyeing steps, indicate that the lightness (L*) increase by reusing dye solution for wool dyeing. The chroma (C*) are also decrease by reusing the dyebath. The hue angles of dye solution change less than the lightness (L*) and chroma (C*).

The results of dyeability are summarized in Table 1 and figure 4 as different dye concentration in initial solution and exhausted dyebath. The results indicate that The dye exhaustion in second stage (wool dyeing with exhausted dyebath) are poor than first stage. The dye exhaustion is a function of mordant concentration. As shown in Figure 4, The dye absorption are increased with increase the mordant concentration.

5. Acknowledgement

6. Reference

[1] M.M. Kamel, Reda M. El-Shishtawy, B.M. Yussef, H. Mashaly;" Ultrasonic assisted dyeing III. Dyeing of wool with lac as a natural dye"; Dyes and Pigments 65, 103-110, 2005.

[2] Jenny D., " The craft of natural dyeing:, Search Press Ltd. , spain ,1994.

[3] Daniela Cristea, Gerard Vilarem;" Improving light fastness of natural dyes on cotton yarn"; Dyes and Pigments 70, 238-245,2006.

[4] Daniela Cristea, Gerard Vilarem;" Improving light fastness of

natural dyes on cotton   yarn"; Dyes and Pigments 70 238-245 , 2006.

[5] Rita, j., " Natural dyes and home dyeing" , Dover Publication, INC. , New York, 1971.

[6] Jenny D., " The craft of natural dyeing:,   Search Press Ltd. ,1994.

[7] Robertson, M. ," Dyes from plants", Litton Educational Publishing Inc.,1973.

[8] Gary, N. M;   "Modern Concepts of Color and Appearance"; Science Publishers Inc. U.S.A, 2000.

[9] .H. Logan ; "UV and Visible Spectrophotometry in Organic Chemistry"; http://members.aol.com/logan20/uv.html; 1997.

[10]   Unknown, "Spectrophotometric Analysis" ; http://www.chem.queensu.ca/ PROGRAMS/UG/Firstyearlabs/apsc100/manual.htm

[11]   Unknown, "Beer's Law"; http://www.serverlogic3.com/lm/rtl3.asp?si=1&k=t%20vs .

[12]   Warren J. Jasper, Eva T. Kovacs, and Gordon A. Berkstresser IV; " Using neural networks to predict dye concentrations in multiple-dye mixtures"; Textile Researcher Journal; 63(9); 545-551;1993.

[13]   M. Marjoniemi and E. Mantysalo; " Neuro-fuzzy modeling of spectroscopic data, part A: modeling of dye solutions"; J.S.D.C. ; Vol.113; 13-17; 1997.

[14]   M. Marjoniemi and E. Mantysalo; " Neuro-fuzzy modeling of spectroscopic data, part B: Dye concentration prediction"; J.S.D.C. ; Vol.113;64-67; 1997.