

Investigation of the dyeing properties of wool fabrics with *Alkanna tinctoria* root extract

Ferda Eser^{1*}, Adem Onal², Firdes Oztav²

¹Suluova Vocational Schools, Amasya University, TR-05500, Amasya/Turkey

²Department of Chemistry Science & Art Faculty, Gaziosmanpasa University, Tokat/Turkey

Abstract

In this work, dyeing properties of wool samples with *Alkanna tinctorum* root extract was investigated. For this purpose, two different dyestuff extracts, red and blue are gained from its roots with acetone and ethanol solvents, as well. Wool fabrics (194 pieces) dyed with $\text{AlK}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, AgNO_3 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mordants at pH 2, 4, 6 and 8, respectively. Unmordanting, pre-mordanting, meta-mordanting, and post-mordanting methods were used for the dyeing experiments. In addition, wool fabrics were pretreated with artificial animal urine system (AAUS) including NH_3 (3%, v/v), CaC_2O_4 (3%, m/v) and urea (3%, m/v) before dyeing processes in order to see the improvement in the fastness properties of the dyed samples with meta-mordanting method. The color codes were determined with Pantone Color Guide, and also washing-, rubbing fastness levels were evaluated using gray scale. According to the evaluations, it is observed that AAUS mordant system helps to improve the light fastness values in general. Good results were obtained both for the dyeings with red and blue components, as well. Optimum dyeing parameters were also evaluated for wool fabric in terms of usage in textile industry.

Article History

Received 31.08.2020

Accepted 07.12.2020

Keywords

Alkanna tinctorum,
Artificial animal urine
system,
Dyeing,
Fastness,
Mordant,
Wool

1. Introduction

Dyes have a wide range of usage including textile, paper, cosmetic, food, pharmaceutical and leather industry (Kamat and Alat, 1990; Samanta and Agarwal, 2009). The discharge of non-biodegradable colored effluents of textile-dyeing causes water pollution which is regarded as one of the main environmental problems today (Glover, 1995). Because of the synthetic effluents that threaten human life, many researchers start to look for eco-friendly products. Hence, the importance and usage of natural dyes are increasing day by day around the World (Smith and Wagner, 1991). Using of mordant is important in the dyeing of fabric. It

¹Correspondence: ferda.eser@amasya.edu.tr

provides an affinity between the dye and the fabric (Tawfik et al., 2007; Oztav, 2009). Although natural dyes have some limitations they offer more advantages such as renewable sources, minimal health hazards, mild reaction conditions, no disposal problems and harmonization with nature (Singhee, 2020). Moreover, they are non-toxic, non-allergic to skin and non-carcinogenic (Esfahani et al., 2012; Tappenier et al., 2014).

It is known that *A. tinctoria* contains alkannin and shikonin compounds in its roots which are responsible for coloration and biological activities, as well (Kourounakis et al., 2002; Rekaby et al., 2009). Shabbir et al. (2019) studied the dyeing potential of *A. tinctoria* root extract on wool yarns. Another study was carried out by Shabbir et al. (2020) including determination of color characteristics and antibacterial properties of *A. tinctoria* and other plant on woolen yarns. The dyeing performances of *A. tinctoria*, *Acacia catechu*, and *Curcuma longa* combinations were investigated on cotton and silk fabric without any additives (salt, mordant, etc.) for eco-friendly colorant resources (Jose et al., 2017). The dyeing of cotton fabric was performed by pad-steam dyeing technique using various mordants (Khattak et al., 2015).

The dyestuffs of *A. tinctoria* -alkannin and shikonin- had been detected in the root of the plant (Papageorgiou et al., 1999). Shikonin is a light red naphthoquinone pigments of *Lithospermum erythrorhizon* plant cells. Alkannin is the first pigment material to be isolated from the root of the aviary plant and is considered to be an essential element of dark red pigments. It is used in food and cosmetic industry for coloration, as well (Khattak et al., 2015).

In 1935, the extracts of shikonin and alkannin were found to be the enantiomer of each other. Alkannin and shikonin and their derivatives have been known to have antitumor activity over the past 25 years, which has prevented tumor formation in some skin cancers in cancer treatment (Zhang et al., 2018).

A. tinctorum is used in the pharmaceutical industry, in cosmetics, and in the dyeing of liquors. Furthermore, extracts prepared from *A. tinctorum* with fennel, cinnamon, rosemary, cumin, black pepper and olive oil are used in rheumatic diseases (Baytop, 1984). Its roots are used in vegetable dyeing (Kayabasi et al., 2000; Dogan et al., 2003) and also has been used in the dyeing of wool carpet yarn with some mordants (Onal, 1996).

In this research, we aimed to investigate the dyeing potential of *A. tinctoria* extract on wool fabrics under different conditions. Besides, we targeted to determine the optimum dyeing conditions for wool fabrics dyed with *A. tinctoria* root extract using both some metal salts and Article Animal Urine System (AAUS), which was developed in our research group before.

2. Materials and Methods

2.1. Reagents and Equipment

All chemicals used in this work were purchased from Merck. Distilled water was used for all steps. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Merck. Extraction was performed by soxhlet apparatus. The mordanting and the dyeing procedures were carried out in a Termal HT 610NHT model dyeing machine. Color codes were determined by Pantone Color Guide. The washing, rubbing (wet, dry) and light-fastness tests of all dyed samples were established according to ISO 105-C06 and to CIS, respectively, and fastness values were determined by Atlas Weather-ometer, a Launder-ometer and a 255 model crock-meter, respectively (Eser and Onal, 2015).

2.2. Dyestuff Extraction from A. tinctoria Root

Ethanol and acetone were determined as the extraction solvents for the extraction of the blue and red components from *A. tinctoria* roots according to TLC spots. For this purpose, 80 g sample was extracted with ethanol (1 L x 3) for 30 minutes, at room temperature. Same procedure was repeated with acetone, as well. Extraction of the blue component was achieved with ethanol extraction and the red component was gained in the presence of acetone. After the evaporation of the solvents, the yield of crude extracts (dye) were found as 3.6% and 2.6% for ethanol and acetone extraction, respectively. The dye bath was prepared at a 30:1 liquor ratio containing 0.5% of dye.

2.3. Dyeing Procedures

The 7x7 cm² of wool fabrics were dyed with the blue solution (ethanol extract) and the red solution (acetone extract), respectively. The dyeing procedures were carried out using the pre-mordanting, meta-mordanting, and post-mordanting methods with $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, AgNO_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mordants at various pH values (pH: 2, 4, 6, and 8). The effect of AAUS mordant at different pH values (pH: 2, 4, 6 and 8) was investigated in terms of high fastness values on wool fabrics.

2.3.1. Dyeing of fiber material by unmordanting method

For unmordanting dyeing of fiber material, 1 g of wool fabric sample was put into the 100 mL of dye solution. The dyeing of the wool fabric was performed at its boiling point for 1 hour. After the end of the process, the fabric was cooled, rinsed with distilled water and air-dried.

2.3.2. Dyeing of fiber material by pre-mordanting method

1 g of fiber material (wool fabric) was treated with 0.1 M, 100 mL of mordant solution for 20 minutes and then filtered. The mordanted fabric was dyed with the dye solution for 1 hour at pH 2. Then it was cooled, filtered and rinsed. The same process was repeated in the same way at pH: 4, 6, 8, respectively.

2.3.3. Dyeing of fiber material by meta-mordanting method

Both mordant (in solid state which is equivalent to 0.1 N 100 mL mordant solution) and dyestuff solution poured into a flask and the pH was adjusted. The fabric was placed into the mixture and it was dyed at its boiling point for 1 h. Finally, it was cooled, filtered and rinsed.

2.3.4. Dyeing of fiber material by post mordanting method

Plant extract (100 mL) was taken into an Erlenmeyer and pH was adjusted. The dyeing of the fabric was carried out at its boiling temperature for 1 hour. After the end of the process, the fabric was rinsed with distilled water and mordanted with mordant solution

(0.1 M 100 mL) for 20 minutes, at its boiling point. Then, it was cooled, filtered, and rinsed.

2.3.5. Dyeing of fiber material with AAUS mordant

Fiber sample (wool fabric, 1 g) kept in AAUS for 24 hours. For this purpose, meta-mordanting method was used for its time-saving and economic properties.

3. Results and Discussion

3.1. Dyeing Results with Red Component

Experimental results of 97 pieces of wool samples dyed with red component using $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, AgNO_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and AAUS mordants according to the pre-mordanting, meta-mordanting, and post mordanting methods are given in Table 1. Generally, good fastness values were obtained in the dyeing of wool fabrics with the red component. The washing fastness was found to be moderate to outstanding (3-5) in all mordanting methods, mordants, and pH values except the dyeing with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, using pre-mordanting method at pH 2. It is known that washing fastness value of the dyed sample depends on the diffusion rate of the dye and concentration of the dye within the fiber (Jothi, 2008). Among the samples, the dyeings with copper mordant ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) using post-mordanting method and the dyeings with iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) using meta-mordanting method gave the best results at all pH values. This can be explained by the coordination tendency of the dyed wool fabrics (Hou et al., 2013) whereas copper (II) and iron (II) can form complexes with the wool fiber on one site and with phenolic colorants of the extract on the other site. According to the data obtained, all the dyed wool samples showed considerable rubbing fastness degrees in both dry and wet forms while the values of the rubbing fastness ranged from 3 to 5, i.e., moderate to outstanding (Table 1). Satisfactory rubbing fastness results can be observed with iron mordant using post-mordanting method, AAUS mordant, and alum mordant ($\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) with meta-mordanting method, as well. It is difficult to obtain high light fastness values in natural dyeing. Generally, good results were observed in the dyeing of wool fibers with the red component of *A. tinctoria*. The lowest grade (3) was recorded with alum mordant. This may be due to formation of a complex with the metal salts which protects the chromophore to

minimum photolytic degradation (Ali et al., 2009). Alkannin and shikonin contain –OH groups in their chemical structures. Previous studies revealed that, two hydroxyl groups give good fastness values due to the increase or decrease of electron density through the substituent may accelerate oxidation (Ali et al., 2009; Kanchana et al., 2013). Excellent light fastness values (7) were also obtained especially with iron mordant using AAUS and post mordanting methods at acidic pH levels. Good light fastness could be easier to transfer the excitation energy from the dye molecule to the macromolecular fiber chains due to the strong dye-fiber bond. The dye–fiber bond thus provides a bridge for transferring the energy of excitation between the two components of the dye molecule and the fiber-ambient system. If this bond facilitates energy transfer, the light fastness increases (Shabbir et al., 2017). It is observed that, AAUS mordant system especially improves light fastness values. The results of the study revealed that pH of the dyeing solution changes the fastness values, but it is not a determinative factor as well (Table 1).

Table 1. Fastness values of wool samples dyed with red component

	Pre-mordanting				Meta-mordanting				Post-mordanting				AAUS				
	pH	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light
CuSO₄·5H₂O	2	3	4-5	3-4	4	4	5	4-5	4	5	5	5	4	4-5	5	4-5	4
	4	3	5	4	4	5	5	4-5	4	5	4-5	4-5	7	5	5	4-5	5
	6	3-4	3-4	3	5	5	5	4-5	4	5	5	4-5	4	5	5	5	4
	8	5	5	3-4	5	5	5	5	6	5	5	5	3	5	5	5	4
FeSO₄·7H₂O	2	4-5	4-5	3-4	6	5	5	4	6	5	5	4-5	7	5	5	5	7
	4	3	5	4	4	5	5	4-5	4	5	5	4-5	7	4-5	5	5	7
	6	3-4	3-4	3	5	5	5	4-5	3	4	5	4-5	5	5	5	5	4
	8	4	5	3-4	5	5	5	4-5	5	4	5	4-5	3	5	5	5	4
K₂Cr₂O₇	2	3	5	5	4	3	5	5	4	3	5	5	4	4-5	5	5	4
	4	3	5	5	5	3	5	4-5	4	4	5	4-5	3	4	5	4-5	3
	6	5	5	4-5	3	4	4-5	4-5	3	3	5	5	3	3-4	5	3-4	3
	8	4	5	4-5	3	3	5	5	5	3-4	5	5	3	3-4	5	5	7
AlK(SO₄)₂·12H₂O	2	3	5	4-5	3	3	5	5	3	4	5	4-5	3	3-4	5	4-5	3
	4	3-4	5	4-5	3	3	5	5	3	3-4	4-5	4	3	3-4	5	4-5	3
	6	4	5	4-5	4	4	5	5	3	4	4-5	4-5	3	3-4	5	5	3
	8	4	5	4-5	3	3	5	5	3	4	5	5	3	3-4	5	4	3
AgNO₃	2	3-4	5	4	5	3-4	4-5	4	3	4	5	4-5	6	3	4-5	4	5
	4	3	5	4	7	3-4	4-5	4	4	4	5	4-5	6	3-4	4	4	5
	6	3-4	5	4-5	5	3-4	4-5	4-5	5	3-4	4-5	4-5	5	3-4	4	3-4	5
	8	4	5	4	5	3-4	5	4	4	4	4-5	4-5	6	4-5	4-5	4	7
CoCl₂·6H₂O	2	2-3	5	4-5	6	3	5	4-5	3	5	5	4-5	3	4	4-5	4-5	4
	4	3	5	4	5	5	5	5	3	5	5	5	3	5	5	4-5	3
	6	3-4	5	4	3	5	5	5	3	4	5	4-5	3	5	5	4-5	3
	8	5	4-5	4	5	5	5	5	4	5	5	4-5	3	4-5	5	5	5

3.2. Dyeing Results with Red Component

Wool samples (97 pieces) were dyed with blue component under similar dyeing conditions for the red component and high fastness values were gained. The fastness values of the wool samples with the blue component using the pre-mordanting, meta-mordanting, and post-mordanting methods are given in Table 2. Although, pH of the medium effects the fastness values, type of mordant is more effective than pH value on the fastness values of the dyed samples. AAUS mordant system changes fastness quality, but it is not the basic criteria especially for the dyeing with blue component (Table 2). Generally, considerable fastness values were obtained with *A. tinctoria* extracts. Washing fastness degree ranges between 3 and 5, i.e., moderate to outstanding. $K_2Cr_2O_7$ mordant gave the best washing fastness results along with meta-mordanting, post-mordanting, and AAUS mordanting systems, as well. The rubbing fastness values range between 4 and 5, i.e., very good to outstanding. Outstanding rubbing fastness values were obtained with alum (meta- and post-mordanting), copper (pre- and post-mordanting), iron (meta-mordanting), and $K_2Cr_2O_7$ (post-mordanting) mordants at all pH values. For the light fastness, fading was taken as a criterion for the determination of the light fastness values of all the dyed samples. The light fastness ranges between 3 and 7, i.e., fair to excellent. Outstanding light fastness values were gained with AAUS mordanting system with $CoCl_2 \cdot 6H_2O$ mordant.

Generally, color tones of purple and blue were obtained in the dyeing of wool fibers with the red component while blue and cream tones were gained with the blue component (Table 3). The results show that the pH values of the dye bath have considerable effects on the dyeing of wool fabrics with all extracts. The effect of the dye bath can be attributed to the relationship between the natural dye structures and the structure of the wool fibers (Mansour et al., 2020). The dyeing with $AgNO_3$ mordant gave generally brown tones. It is concluded that, mordants, mordanting methods, and pH values are effective in the color hue, as well. When all the parameters were evaluated, the most suitable dyeing conditions for wool fabric samples dyed with blue component seems the dyeing with $FeSO_4 \cdot 7H_2O$ mordant using the post-mordanting method at pH = 2, and the dyeing by using the $FeSO_4 \cdot 7H_2O$ and $K_2Cr_2O_7$ mordants with meta-mordanting method at pH = 4, as well. When the relationship between fastness and pH for wool samples were examined, it was seen that the fastness increases when the pH decrease. The optimum pH value for wool samples was determined as 2 and 4, respectively. This is due to the fact that the wool fiber is protein. Protein fibers exhibit an














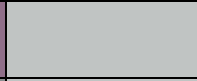












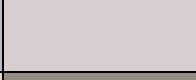





















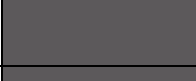



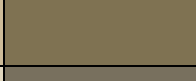


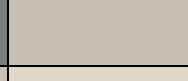






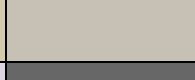













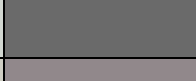











amphiprotic feature. Due to its chemical structure (because it contains free amino and carboxyl groups), wool has high affinity for both mordant and dyestuff. Under acidic conditions, all the cationic groups in wool are potential sites for the attraction of negatively charged, anionic acid dyes to wool. The negative charge on wool under alkaline conditions (above pH 8) makes the fiber substantive to dyes that carry a cationic charge (basic dyes). Since natural dyes used are sparingly soluble in water, containing OH groups, they interact ionically with the protonated terminal amino groups of wool fabric at acidic pH via ion exchange reaction because of the acidic character of the OH groups (Mansour et al., 2019). Oxo chrome groups in natural dyes can be directly bound to wool. This binding is caused by electrostatic pulling of the opposite loads in wool and dyestuffs. The ionic amino groups are also released as the decomposition of carboxyl groups decreases below of the isoionic pH. These amino acids combine with acid anions to form salt.

In this salt quickly decomposed and dyestuff anion passes to instead of the acid anion. The dyestuff anions form more resistant salts with wool molecules than their acid roots. This is explained by the binding of dyes to the wool molecule not only by electrostatic gravitational forces, but also by intermolecular bonds such as hydrogen bond, dipole-dipole interaction. The formation of salt bridge bonds between the ammonium and carboxyl groups at the isoionic point enhances the staining of the wool fibers at this pH. Therefore, the wool is more suitable to be stained in acidic environment at pH below isoionic point. Our experimental work has supported this information. Dyestuffs are not preferred in the basic environment because the dye decomposition of the dyestuffs will decrease and the dyes cannot be attached to the wool.

Table 2. Fastness results of wool samples dyed with blue component

	Pre-mordanting				Meta-mordanting				Post-mordanting				AAUS				
	pH	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light	Washing	Rubbing (dry)	Rubbing (wet)	Light
CuSO ₄ ·5H ₂ O	2	3-4	5	5	4	5	5	5	4	5	5	5	5	4-5	5	4-5	4
	4	3	5	5	4	4-5	5	5	4	5	5	5	5	5	5	5	4
	6	5	5	5	4	5	5	5	3	5	5	5	5	5	5	5	6
	8	3-4	5	5	4	5	5	4-5	4	5	5	5	5	5	5	4-5	3
FeSO ₄ ·7H ₂ O	2	3-4	5	5	5	5	5	5	6	5	5	5	7	4-5	5	5	5
	4	4	5	4-5	6	5	5	5	7	5	5	4-5	7	5	5	4-5	6
	6	4	5	5	5	4-5	5	5	6	5	5	4-5	7	4-5	5	4-5	6
	8	5	5	5	3	5	5	5	5	4-5	5	4-5	5	5	5	4-5	7
K ₂ Cr ₂ O ₇	2	3	5	5	5	5	5	5	6	5	5	5	6	5	5	5	6
	4	3-4	5	4-5	4	5	5	5	7	5	5	5	5	5	5	5	6
	6	4	5	5	4	5	5	4-5	6	5	5	5	5	5	5	4-5	4
	8	5	5	5	4	5	5	5	4	5	5	5	6	5	4-5	4	4
AlK(SO ₄) ₂ ·12H ₂ O	2	3	5	4-5	3	3-4	5	5	6	4-5	5	5	5	5	5	5	3
	4	4	5	4-5	3	3-4	5	5	6	3-4	5	5	4	4	5	4-5	3
	6	4	5	5	3	3-4	5	5	4	5	5	5	4	5	5	4-5	3
	8	5	5	5	3	3-4	5	5	4	5	5	5	4	5	5	4-5	3
AgNO ₃	2	3-4	5	5	5	3-4	5	4	4	3-4	4-5	4-5	4	3-4	4-5	3-4	5
	4	3-4	5	5	6	4	4	4	3	4-5	5	4	4	3-4	4	4	6
	6	3	5	4-5	5	3-4	4	4	5	3	4	4	6	3-4	4	4	7
	8	5	5	4	5	4	4-5	4-5	4	3-4	4-5	4	4	3-4	4	3-4	6
CoCl ₂ ·6H ₂ O	2	3	5	5	5	5	5	5	4	4-5	5	5	5	5-4	5	4-5	7
	4	3-4	5	5	6	5	5	4-5	4	4-5	5	4-5	4	4	5	5	7
	6	3-4	5	5	5	4	5	5	5	4	5	4-5	4	4	5	4-5	7
	8	3-4	5	5	4	3-4	5	4-5	6	4-5	5	4-5	3	5	5	4-5	7

Table 3. Colors of the dyed samples

unmordaned									
	pH	Pre-mordanting		Meta-mordanting		Post-mordanting		AAUS	
		Red comp.	Blue comp.	Red comp.	Blue comp.	Red comp.	Blue comp.	Red comp.	Blue comp.
CuSO₄·5H₂O	2								
	4								
	6								
	8								
FeSO₄·7H₂O	2								
	4								
	6								
	8								
K₂Cr₂O₇	2								
	4								
	6								

	8								
AlK(SO₄)₂·12H₂O	2								
	4								
	6								
	8								
AgNO₃	2								
	4								
	6								
	8								
CoCl₂·6H₂O	2								
	4								
	6								
	8								

3.3. Dyeing Mechanism

The mechanism of wool dyeing by pre-mordanting can be explained as follows. The pre-mordanting method consists of 2 steps. Firstly, the cation in the metal salt used as mordant forms a complex compound by binding on the free amino and carboxyl groups in the wool with a coordinative bond. The metal cation, which is then bonded to the wool by the coordinative bond with oxygen and nitrogen atoms, stabilizes the dye to the fibers by making a coordinative bond with the binding groups such as -OH in the dye molecule and the basic color of the wool is released after this step (Onal, 2000).

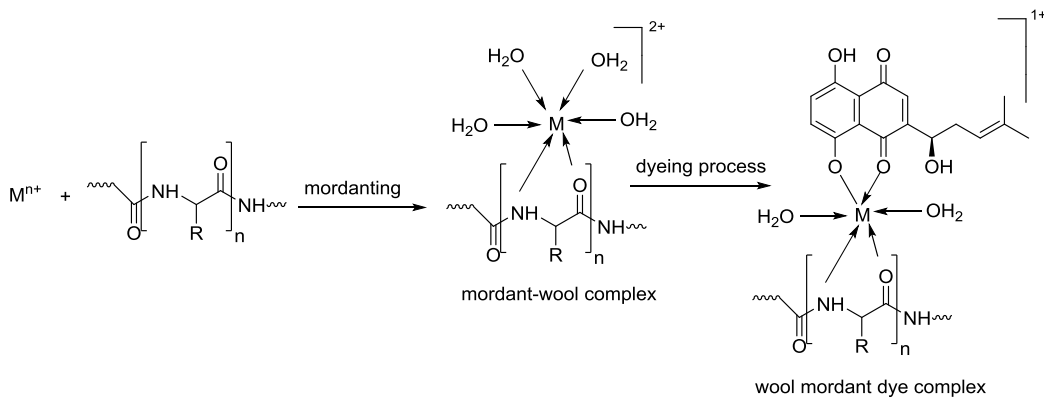


Figure 1. Dyeing mechanism of wool samples with pre-mordanting method [M: metal salt (iron mordant)]

The dyeing mechanism of dyed wool samples with pre-mordanting method is seen in Figure 2.

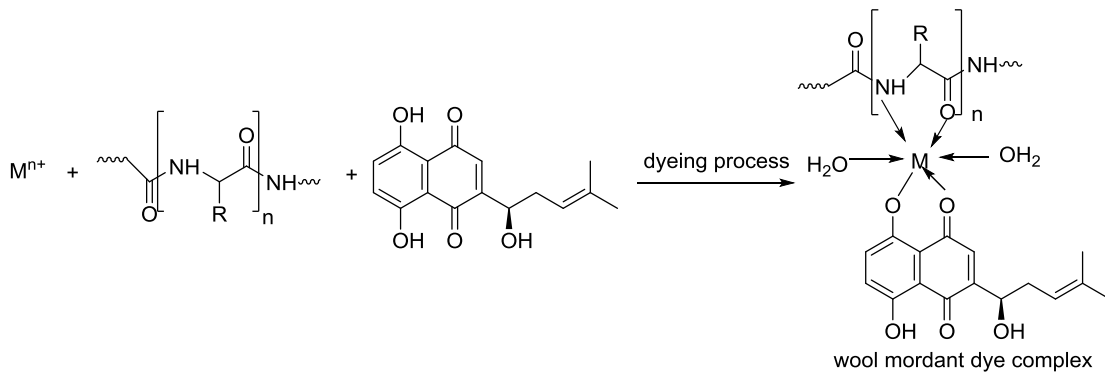


Figure 2. Dyeing mechanism of the wool samples with meta-mordanting method [M: metal salt (iron mordant)]

The dyeing of wool samples occurs one step for together mordanting method is seen in Figure 3.

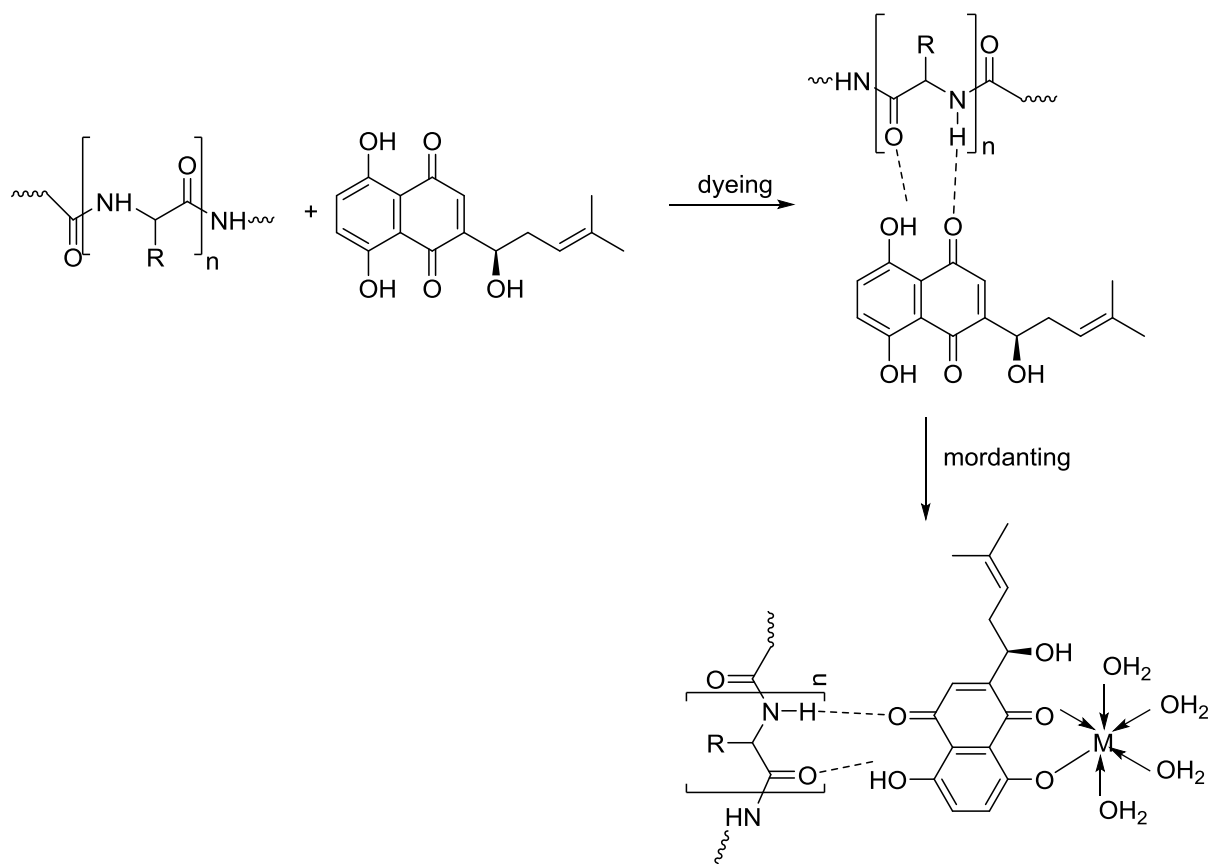


Figure 3. The dyeing mechanism for wool samples with post-mordanting method [M: metal salt (iron mordant)]

The dyeing mechanism of the wool samples with last mordanting method is carried out in two steps. The wool is first dyed with dyestuff, then is mordanted with the metal cation used as mordant. The main color of the wool (Onal, 2000) is revealed by the binding in the last step, it is seen in Figure 3.

The complexes formed by the cation in the metal salt used as mordant by binding to the amino group in the protein fiber can be bound to the dye molecule as seen in the mechanisms, as well as from the O atom in the lower -OH and carbonyl groups, but sterically it is more difficult to bind and more energy requires. Therefore, when forming mechanisms, it was assumed that the dyestuff is bound at the top of the molecule by O atoms in the OH and carbonyl groups, where the steric barrier is the least.

The ideal dyeing temperature for wool is 80 °C while the period is 45-60 minutes. In case of high temperatures for wool, the structure of keratin will be damaged, it causes wrinkle and felting in wool fibers. In this study, fiber samples were dyed in the ideal temperature range in the ideal time period as seen in the tables.

Blue, navy blue, magenta, green, brown, gray and lead color and color shades are obtained with red compound; purple, blue, navy blue, brown, pink, beige color and color tones are obtained with blue compound. The fastness analyses of dyed fabrics are high and the colors obtained are bright and vivid.

Different colors and color tones were obtained in the dyeing of wool fabric with AAUS mordant system, and fastness values were higher than others. This situation can be explained as follows. In this mordant system, ammonia opens the fiber micelle and facilitates the penetration of the dye into the fiber and oxalate stabilizes the complex formed in the environment. Urea increases the solubility of the dyestuff, causing swelling of the fiber, decreases the degree of aggregation (clustering of ions in the environment) and facilitates diffusion.

The rate of diffusion is the transfer rate to the interior of the fiber. The high diffusion ratio allows for quick set-up of the balance and rapid removal of irregularities in the adsorption of the dye. Thus, a system resistant to external influences is formed with AAUS mordant and fastness is high. In addition to this, fiber samples stained with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ mordant were found to have high fastness values. This can be explained by the fact that the iron metal is less than the coordination number and the iron has two different oxidation steps in its compounds.

4. Conclusion

In this study, the *Alkanna tinctoria* roots were used for the dyeing of wool fabrics. Natural dye solution was extracted and applied to the selected fabrics using pre-, meta, and post-mordanting techniques. Blue, navy blue, magenta, green, brown, gray and lead color and color shades are obtained with red compound; purple, blue, navy blue, brown, pink, beige color and color tones are generally obtained with blue compound. The fastness analyses of dyed fabrics are found high and colors are bright and vivid. Fastness of color obtained using artificial

animal urine system (AAUS) was higher than other dyed samples which are unpretreated with AAUS. We can say that the pre-treatment of fabrics with AAUS increases the fastness. Here, ammonia opens the micelles of the fabric, urea increases the solubility of dye and oxalate improves the stability of metal complex. The dyeing results of the study showed that *Alkanna tinctoria* roots can be used as a natural dyestuff source in the dyeing of wool fabrics with suitable mordant.

References

- Ali, S., Hussain, T., Nawaz, R. 2009. Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method, *Journal of Cleaner Production*, 17(1): 61-66.
- Baytop, T. 1984. Treatment with plants in Turkey. Publication of Pharmacy Faculty, Istanbul.
- Dogan, Y., Baslar, S., Mert, H.H., Güngör, A. 2003. Plants used as natural dye sources in Turkey, *Economic Botany*, 57(4): 442-453.
- Eser, F., Onal, A. 2015. Dyeing of wool and cotton with extract of the nettle (*Urtica dioica* L.) leaves, *Journal of Natural Fibers*, 12(3), 222-231.
- Esfahani, H.M., Esfahani, Z.M., Degahki, N.K. Hosseini-Sharifabad, A., Tabrizian, K., Parsa, M., Ostad, S.N. 2012. Anti-inflammatory and anti-nociceptive effects of the ethanolic extracts of *Alkanna frigida* and *Alkanna orientalis*, *Journal of Natural Medicine*, 66(3): 447-452.
- Glover, B. 1995. Are natural colors good for your health—Are synthetic ones better, *Textile Chemist and Colorist*, 27(4): 17-20.
- Hou, X., Chen, X., Cheng, Y., Xu, H., Chen, L. et al. 2013. Dyeing and UV-protection properties of water extracts from orange peel, *Journal of Cleaner Production*, 52: 410-419.
- Jose, S., Gurumallesh Prabu, H., Ammayappan, L. 2017. Eco-friendly dyeing of silk and cotton textiles using combination of three natural colorants, *Journal of Natural Fibers*, 14(1): 40-49.
- Jothi, D. 2008. Extraction of natural dyes from African marigold flower (*Tagetes erecta* L) for textile coloration, *AUTEX Research Journal*, 8(2): 49-53.
- Kamat, S.Y., Alat, D.V. 1990. Natural dyes—A dying craft?, *The Indian Textile Journal*, 3(6): 66-70.
- Kayabasi, N., Sanli, H.S., Etikan, S. 2000. Color obtained *Alkanna tinctoria* and labada and investigation of these colors fastness, *Yuzuncu Yil University Journal of Agriculture*, 10(1):7-10.
- Khattak, S.P., Rafique, S., Hussain, T., Inayat, F., Ahmad, B. 2015. Colour fastness and tensile strength of cotton fabric dyed with natural extracts of *Alkanna tinctoria* by continuous dyeing technique, *Journal of the Chemical Society of Pakistan*, 37(5): 903-909.
- Kourounakis, A.P., Assimopoulou, A.N., Papageorgiou, V.P., Gavalas, A., Kourounakis, P. N. 2002. Alkannin and shikonin: Effect on free radical processes and on inflammation—a preliminary pharmacological investigation, *Archiv Der Pharmazie*, 335(6):262-266.
- Mansour, R., Dhoub, S., Sakli, F. 2020. UV protection and dyeing properties of wool fabrics dyed with aqueous extracts of madder roots, chamomiles, pomegranate peels, and apple tree branches barks, *Journal of Natural Fibers*, 1-11.

- Onal, A. 1996. Extraction of dyestuff from onion (*Allium cepa* L.) and its application in the dyeing of wool, feathered-leather and cotton, Turkish Journal of Chemistry, 20(3): 194-203.
- Onal, A. 2000. Natural dyestuffs. Gaziosmanpasa University, Publishing of Science Faculty, Tokat, Turkey.
- Oztav, F. 2009. Investigation of usage as dyestuff of *Alkanna tinctorum* on dyeing cellulosic and protein fiber. PhD thesis. Gaziosmanpasa University, Institute of Science, Tokat, Turkey.
- Papageorgiou, V., Assimopoulou, N., Couladouros, E., Hepworth D., Nicolaou, K.C. 1999. The chemistry and biology of alkannin, shikonin and related naphthazarin natural products, Angewandte Chemie International Edition, 38: 270-300.
- Rekaby, M., Salem, A.A., Nassar, S.H. 2009. Eco-friendly printing of natural fabrics using natural dyes from alkanet and rhubarb, The Journal of the Textile Institute, 100(6): 486-495.
- Samanta, A.K., Agarwal, P. 2009. Application of natural dyes on textiles, Indian Journal of Fibre & Textile Research, 34: 384-399.
- Shabbir, M., Rather, L.J., Azam, M., Haque, Q.M.R., Khan, M.A. et al. 2020. Antibacterial functionalization and simultaneous coloration of wool fiber with the application of plant-based dyes, Journal of Natural Fibers, 17(3): 437-449.
- Shabbir, M., Rather, L.J., Bukhari, M.N., Shahid-ul-Islam, Khan, M.A. et al. 2019. First-time application of biomordants in conjunction with the *Alkanna tinctoria* root extract for eco-friendly wool dyeing, Journal of Natural Fibers, 16(6): 846-854.
- Shabbir, M., Islam, S.U., Bukhari, M.N., Rather, L.J., Khan, M.A. et al. 2017. Application of *Terminalia chebula* natural dye on wool fiber—evaluation of color and fastness properties, Textiles and Clothing Sustainability, 2(1): 1-9.
- Singhee, D. 2020. Review on natural dyes for textiles from wastes. In: Samanta, A.K., Awwad, N., Algarni, H.M. (Eds). Chemistry and Technology of Natural and Synthetic Dyes and Pigments. IntechOpen.
- Smith, R., Wagner, S. 1991. Dyes and the environment is natural better?, American Dyestuff Reporter, 80(9): 32-34.
- Tappenier, J., Vasiliou, A., Ganzera, M., Fessas, D., Stuppner, H. et al. 2014. Quantitative determination of alkannins and shikonins in endemic mediterranean species, Biomedical Chromatography, 28(7): 923-933.
- Tawfik, W.A., Shams, K.A., Abdel-Azim, N.S., Hassan, N.M., Ismail, S.I. 2007. Naphthaquinones of *Alkanna orientalis* (L.) Boiss., African Journal of Traditional, Complementary and Alternative Medicines, 4(1): 55-58.
- Zhang, X., Cui, J.H., Meng, Q.Q., Li, S.S., Zhou, W. et al. 2018. Advance in anti-tumor mechanisms of shikonin, alkannin and their derivatives, Mini Reviews in Medicinal Chemistry, 18(2): 164-172.