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DYEING OF SILK IN EDIRNE RED COLOR WITH MADDER

İsmail YÜCE *

Nilgün BECENEN *

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Abstract: Silk is a natural filament obtained from the Bombyx mori species of silkworm, with a fiber length of up to 3000 meters. During the Ottoman era in Edirne, sericulture and silk trade were important activities. To this end, silk factories, trade centers, and silk weaving schools were established, creating an important source of income for the people of Edirne.

Edirne Red is a natural dye obtained from the *Rubia Tinctorum* L. plant and is part of the Ottoman Empire's heritage. This dye is resistant to sunlight and washing. It has been used in Turkish carpets, as well as in silk and cotton fabrics.

The aim of this study is to bring together the importance of Edirne Red and silk in Edirne's history. For this purpose, 100% silk fabrics were dyed using madder (*Rubia Tinctorum* L.) grown within the borders of Edirne province. The effects of dye ratios and auxiliary chemicals used on color and colorfastness were examined during the dyeing process. The color values of the fabrics were measured numerically in the CIEL*a*b* color space, and the washing and light fastness values of the dyed fabrics were also measured. Additionally, high-performance liquid chromatography (HPLC) analyses were performed on both the used madder and the dyed fabric.

Based on the obtained data, the closest Edirne Red color was achieved by pre-mordanting fabric before dyeing and using ethanol as the dye solvent. Madder dye, successfully applied to silk fabrics under different conditions, has shown good results in terms of color yield and fastness properties.

Keywords: Edirne Red, Silk, *Rubia Tinctorum* L., Madder, Fastness

İpeğin Kök Boya İle Edirne Kırmızısı Rengine Boyanması

Öz: İpek, bombyx mori türü ipek böceğinden elde edilen ve lif uzunluğu 3000 m.ye kadar ulaşabilen doğal bir filamenttir. Osmanlı dönemi Edirne'sinde, ipek böcekçiliği ve ticareti önemli bir yer tutmuştur. Bu amaçla, ipek fabrikaları, ticaret hanı, ipekçilik okulu kurulmuş ve Edirne halkı için ipek önemli bir gelir kaynağı yaratmıştır. Edirne Kırmızısı, *Rubia Tinctorum* L. bitkisinden elde edilen doğal bir boyadır ve Osmanlı imparatorluk mirasıdır. Bu boya güneş ışığına ve yıkamaya karşı dirençlidir. Türk halılarında, ipek ve pamuklu kumaşlarda kullanılmıştır.

Yapılan bu çalışmada Edirne tarihinde önemli yer edinen Edirne kırmızısını ve ipekçiliği bir araya getirmek amaçlanmıştır. Bu amaçla, Edirne ili sınırları içerisinde yetişen *Rubia Tinctorum* L. kök boya bitkisi kullanılarak %100 ipekli kumaşlar boyanmıştır. Boyama işleminde, boyarmadde oranlarının ve kullanılan yardımcı kimyasalların renk ve haslık üzerindeki etkileri incelenmiştir. Elde edilen boyamalar sonucunda CIEL*a*b* renk alanında kumaşların renk değerleri sayısal olarak ölçülmüş ve aynı zamanda boyalı kumaşların yıkama ve sürtme haslık değerleri analiz edilmiştir. Aynı zamanda kullanılan kök boyarmaddenin ve boyanmış kumaşın yüksek performanslı sıvı kromatografisi (HPLC) analizleri gerçekleştirilmiştir.

* Edirne Vocational School of Technical Sciences, Trakya University, 22030, Edirne, Türkiye
Corresponding Author: İsmail YÜCE (ismailyuce@trakya.edu.tr)

Elde edilen veriler ışığında, kumaşın boyamadan önce ön mordanlama yapılması ve boyarmadde çözücüsü olarak etanol kullanılması sonucu en yakın Edirne kırmızısı rengi elde edilmiştir. İpekli kumaşlara farklı koşullarda başarıyla uygulanan kök boya, renk verimi ve haslık özellikleri açısından iyi sonuçlar vermiştir.

Anahtar Kelimeler: Edirne Kırmızısı, İpek, *Rubia Tinctorum* L., Kök boya, Haslık

1. INTRODUCTION

Edirne, known with the prefix "Edirne" worldwide, is a city that stands out as one of the rare cities with a distinct color. One of the cultural values of Edirne province is the Edirne Red, known as "Rouge d'Andrinople" in French. Edirne Red, initially referred to as Turkish Red because it was brought to Europe from Turkey in the 1740s, represents a lengthy and laborious dyeing process, also known as "Rouge d'Andrinople" in international literature (Akman, 2021).

This color holds significant importance in the European textile industry as a historical color. The red colors observed in Byzantine-origin icons, Egyptian (8th-18th century) and Ottoman fabrics have been identified through HPLC analysis and found to be derived from *Rubia Tinctorum* L. (Karapanagiotis, and Karadag, 2015; Karapanagiotis et al., 2021).

Rubia tinctorium L. is a natural source of dye and in the anthraquinone dyestuff class. The roots of the plant contain various dye substances from a chemical perspective. These include alizarin, rubiadin, purpurin, xanthopurpurin and munjistin. The plant has been recognized as the most popular source of red color tones and has also contributed to obtaining shades of pink, orange, purple, gray, and brown with high color intensity (Singh et al., 2020).

Rubia tinctorium L. is extracted from the dried roots of the plant. In silk dyeing, a metallic salt called mordant is required for satisfactory dyeing and color fastness properties, as well as to achieve different shades of color (Kasiri and Safapour, 2015).

Silk is one of the most preferred high-quality textile materials due to its soft, shiny, excellent absorbent, draping, elegant appearance, and superior comfort. Unfortunately, its very low wet elasticity causes significant inconvenience in the use of silk textiles as they easily wrinkle when washed or get wet at home (Yang and Li,1993). Silk fibers produced by silkworms consist of natural macromolecular proteins called sericin and fibroin. Fibroin is the protein that forms the fibrillar structure of silk and constitutes approximately 70% of raw silk. Sericin, on the other hand, is a water-soluble gum-like protein that surrounds and connects the fibroin fibrils (Pereira, et.al., 2015).

In this study, the two cultural values of Edirne, silk and Edirne red, were brought together. For this purpose, 100% silk fabrics were dyed with a natural dye obtained from madder cultivated in Edirne/Havsa. The effects of the amount of dye and auxiliary chemicals used in the dyeing process on color and fastness were examined. In this study, the effect of the use of auxiliary chemicals in the dyeing of fabrics pre-treated with alum on colors and fastness has been investigated. For this purpose, dyeing and fastness results of fabrics that have been pre-mordanted have been examined by applying oil mordant (Turkey red oil) and metallic mordant (alum) during the dyeing process. Additionally, the effect of adding ethanol to the dyeing bath on color and fastness has been evaluated in this study. Furthermore, dyeing processes were conducted using a dye material derived from roots grown in the location that gives its name to the color 'Edirne Red'. The color values of the fabrics were measured in the CIEL*a*b* color space. The fastness properties of the dyeing processes (washing and light fastness) were analyzed. Additionally, HPLC analyses were conducted on the plant root dye [2].

2. MATERIAL AND METHOD

2.1. Materials

In this study, 100% Silk, woven fabrics are used in the plain construction. The weft density of the fabric is 42 thread/cm, while the warp density is 61 thread/cm. It was purchased from Büyükaşıklar Silk Company. The silk fabric has a width of 140 cm and a weight of 75 g/m^2, and its sericin has been removed. The dye used in the dyeing process was obtained from root plants (*Rubia Tinctorum* L.) collected in the garden of Trakya University Havsa Vocational School, located in Havsa district of Edirne province. These dyes were harvested one year after planting, and the same dye was used for all fabric dyeing. Turkey red oil and aluminum mordant used in the dyeing process. Turkey red oil were purchased from Ataman Kimya Corporation and aluminum mordant were purchased from Natural Dyes Company.

2.2. Method

2.2.1. Madder Production and Dyeing Process

The *Rubia Tinctorum* L. plant, grown in Edirne/Havsa, is initially harvested from the field. The extracted roots are first purified from the soil and then washed with water. The roots are sliced into pieces of 4-5 cm in size and left to dry in a shaded area. After being left outdoors for one week, they are dried in a drying oven at 60-65 °C for 24 hours. Once dried, the roots are ground into powder using a grinder and packaged in a moisture-proof manner. The above-ground part of the plant, along with the roots and the powdered form, are presented in Figure 1.

Figure 1:
The stages of obtaining the madder. Respectively; Above ground, roots and image of dyestuff obtained from roots.

Before the dyeing process, all fabrics were subjected to a pre-mordanting process with 7% aluminum sulfate ($KAI(SO_4)_2 12.H_2O$). This process was carried out at 80°C for 1 hour (Figure 2). After the pre-mordanting process, the fabrics were ready for the dyeing process. Initially, a dye extract was prepared by dissolving 30g of root dye in 1 liter of water. The prepared extract was left to stand overnight and then filtered to complete it to 1 liter. The dyeing process was carried out under the same conditions for all fabrics (Figure 2).

After the dyeing process is complete, samples have been first washed under cold water. Subsequently, the dyed fabrics were washed with a soap solution without bleach at 40°C for 30 minutes. The washed samples were rinsed and hanged to dry.

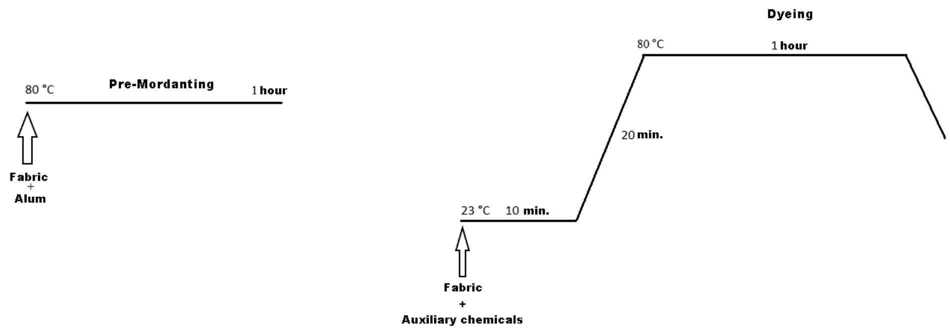


Figure 2:
Pre-Mordanting and Dyeing

The dyed fabrics differ in terms of dye color intensity and the auxiliary chemicals used, with a total of 12 pieces. Table 1 provides the color intensities, chemicals used, and their ratios.

Table 1. Classification of Dyed Fabrics

Fabric Code	Amount of dyestuff	Auxiliary Chemicals		
		Ethanol	Alum	Turkey red oil
I-1	100%	-	-	-
I-2	100%	-	3.3%	-
I-3	100%	-	-	3.3%
I-4	100%	-	3.3%	3.3%
I-5	150%	-	-	-
I-6	150%	-	3.3%	-
I-7	150%	-	-	3.3%
I-8	150%	-	3.3%	3.3%
I-9	100%	20%	-	-
I-10	100%	20%	3.3%	-
I-11	100%	20%	-	3.3%
I-12	100%	20%	3.3%	3.3%

2.2.2. Color Measurement and Colorfastness Tests

The numerical values of the colors of the dyed fabrics were measured with the X-Rite Ci 6x spectrophotometer device. As a result of the measurements, the color's L*, a*, b*, C, hº, R%, and K/S values were obtained from R%.

At the end of the dyeing applications, CIEL*a*b* color values were measured under D65 daylight and a 10° illumination angle. The color intensity values of the samples were calculated using the Kubelka-Munk equation (Equation 1) by using the percent reflectance values (R%) at visible wavelengths (400-700 nm) for each dyeing.

$$\frac{K}{S} = \frac{(1-R)^2}{R^2} \quad (1)$$

In this equation; K represents the absorption coefficient of color, S represents the scattering coefficient of color. %R corresponds to the reflectance (reflection) value of the sample at maximum absorbance. The higher the K/S value, the darker the color becomes. (Yılmaz Şahinbaşkan, et al., 2018).

Washing fastness were conducted on the Gayrowash washing test device (TS- EN-ISO105 C06, 2010). The lightfastness tests were conducted on the Xenotest Alpha (Atlas) Light fastness Testing Device according to TS EN ISO 105-B02, 2013 standard.

2.2.3. HPLC Analyses

The HPLC analyses were conducted at DATU Laboratory located in Istanbul. The percentages of the madder used in the dyeing, namely alizarin, purpurin, munjistin, and rubiadin, have been revealed.

The madder substance in powder form was weighed at 11 mg, and a mixture of hydrochloric acid (HCl), methanol (MeOH), and water (H_2O) in a ratio of 2:1:1 (v:v:v) was added to it. Afterwards, it was hydrolyzed in boiling distilled water for a period of 8-10 minutes. Subsequent to, the solution was cooled under running cold water and evaporated to dryness in a water bath at 65°C using a gentle stream of nitrogen gas. The resulting dry residue was dissolved in 200 µl of a mixture of methanol and water in a ratio of 2:1 (v:v). The solution was then centrifuged at 4000 rpm for 10 minutes, and 50 to 100 µl of the supernatant was injected into the High-Performance Liquid Chromatography (HPLC) apparatus.

3. RESULTS AND DISCUSSION

3.1. HPLC Results

Madder were identified using HPLC analyze. The dyed samples were identified based on the absorption spectra acquired with reference standard compounds. The chromatogram of the madder is presented in Figure 3. Upon examination of the chromatogram, a peak of munjistin was observed at 26.7 minutes. Peaks of alizarin, purpurin, and rubiadin were observed at 28.6, 29.5, and 30.1 minutes, respectively. The spectra of alizarin and purpurin have been compared with the standard in Figure 4 and Figure 5 shows the spectra of four pigments.

When Table 2 is examined, the analyzed pigments, alizarin, have the highest amount (79.77%), while purpurin is the pigment with the lowest ratio (0.68%).

Table 2. The time, area, height, and percentage ratios of the four pigments in madder.

Time	Peak Area	Height	Peak	%
26.753	4333.2	503.2	Munjistin	11.13
28.667	32299.6	3611.6	Alizarin	79.77
29.505	88.1	31.1	Purpurin	0.68
30.127	3888.3	381	Rubiadin	8.42

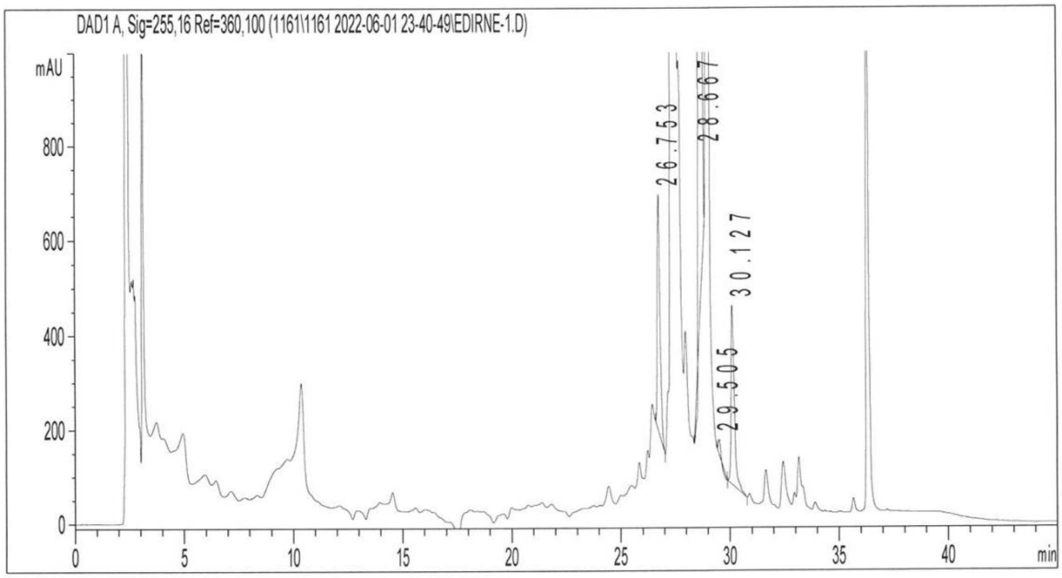


Figure 3:
Chromatogram of Madder

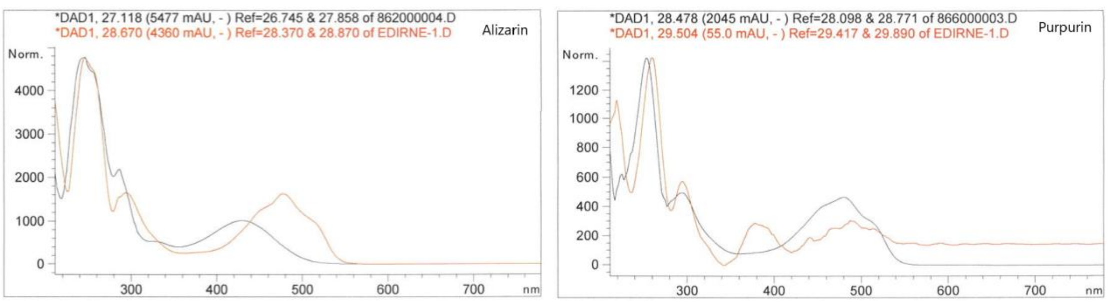
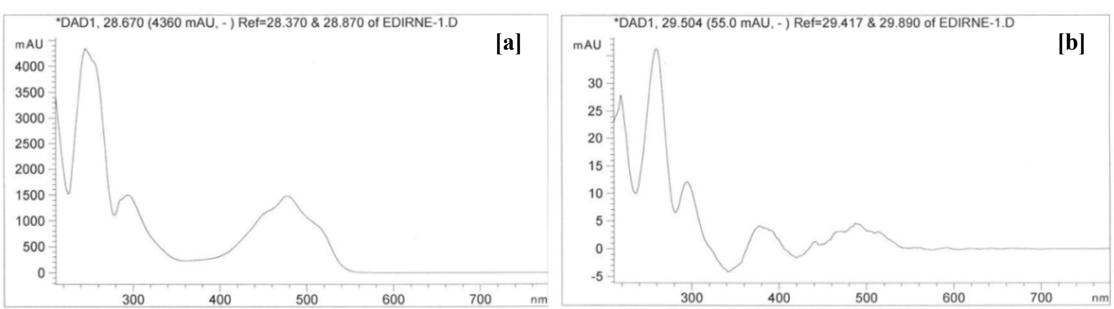


Figure 4:
Spectrum of coloring pigments in madder and comparison with Standard.



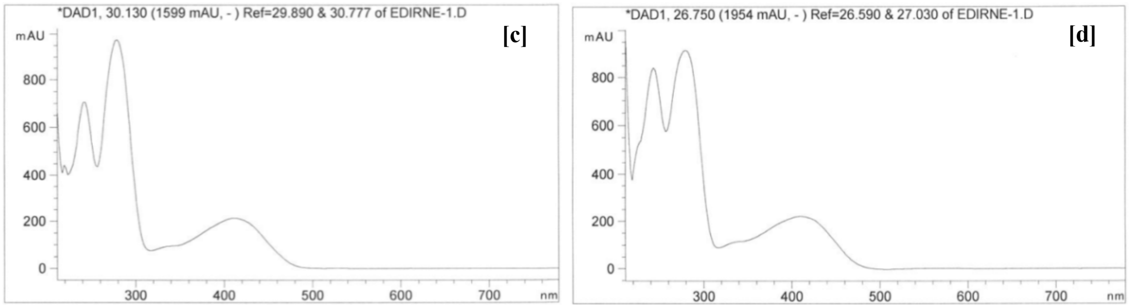


Figure 5:

Spectrum of coloring pigments in madder, [a]: Spectrum of alizarin, [b]: Spectrum of purpurin, [c]: Spectrum of rubiadin, [d]: Spectrum of munjistin.

3.2. Color Values

CIEL*a*b* color values were measured and they were taken at three different locations on the fabric, and the average values are given in Table 3.

Table 3. CIELab values of Dyed Samples.

Code	L*	a*	b*	C*	h°	Samples
I-1	43.79	36.57	26.37	45.38	35.88	
I-2	46.57	33.49	27.61	44.63	37.43	
I-3	43.62	37.98	28.59	48.28	37.19	
I-4	48.55	34.86	27.70	44.86	38.34	
I-5	38.03	39.13	27.47	48.90	34.45	
I-6	40.62	36.73	27.55	47.68	36.94	
I-7	38.58	38.62	28.42	48.90	36.01	
I-8	49.43	32.26	31.68	45.92	44.41	
I-9	40.83	37.82	24.96	46.62	32.83	
I-10	42.70	35.45	27.55	46.22	37.12	
I-11	39.31	38.49	25.96	47.13	33.90	
I-12	47.56	33.42	29.76	45.11	40.45	

When a color is represented in CIELab, L* indicates the lightness-darkness, a* represents the red-green, and b* represents the yellow-blue color values (Cosmulescu et al., 2019). The K/S graphs of the samples within the wavelength range of 400-700 nm have also been plotted (Figure 6). In Figure 7, the effect of ethanol usage on color has been examined by comparing L*, a*, and b* values. At the same time, the two-dimensional coordinate plot has been drawn for the samples based on the color values of a* and b* (Figure 8).

Examining the data in the table 3 and Figure 6, it is observed that the darkest red color is found in sample I-5. The lightest red color is observed in sample I-4 and I-8. When dyeings with the same color intensity were examined, it was observed that the colors of the fabrics treated with alum mordant were lighter. Since all the samples were pre-mordanted with alum mordant before dyeing, it can be interpreted that its addition during dyeing opened up the color compared to the dyeing without alum mordant. It was observed that the use of Turkey red oil relatively affected the color value, but the values were found to be negligible. This result is consistent with the literature (Özer et.al.,2016). It was observed that both Turkey red oil and alum mordant usage lightened the color in all samples.

When the same color intensity and auxiliary chemical usages were compared, it was observed that the use of ethanol darkened the color (Figure 7). Ethanol serves as a solvent in preparing the extract and solvents with high polarity like ethanol have been used for the extraction of madder in many studies (De Santiset.al.2007; Derksen et.al.,1998; Derksen et.al.,2002; Ford et.al.2015; Marhoume et. al.2021). It can be said that due to the increased solubility of dyes in the presence of ethanol, colors are darker. Therefore, it can be concluded that the use of ethanol in dyeing silk with madder will result in more efficient colors.

When the effect of adding ethanol was examined on color, it was observed that a* values generally increased with ethanol (Figure 8). The positive increase in a* value is an indicator of a more intense red color. Therefore, it can be said that the use of ethanol has a positive impact on the color. Since ethanol is used as a solvent, it increases the dissolution of the dye stuff, and it can be said that redder colors are obtained (De Santiset.al.2007; Derksen et.al.,1998).

With the addition of alum, a decrease in the values of a* (red intensity) has been observed. b* values, on the other hand, have increased with the addition of alum (yellow intensity has increased).

The use of Turkey red oil was observed not to cause a significant difference in a* color values; however, it has been observed to increase the b* values (Figure 8). Therefore, it can be said that the addition of Turkey red oil makes the color more yellow. In a study, it has also been observed that the addition of Turkey red oil increases the b* values (Özer et.al.,2016).

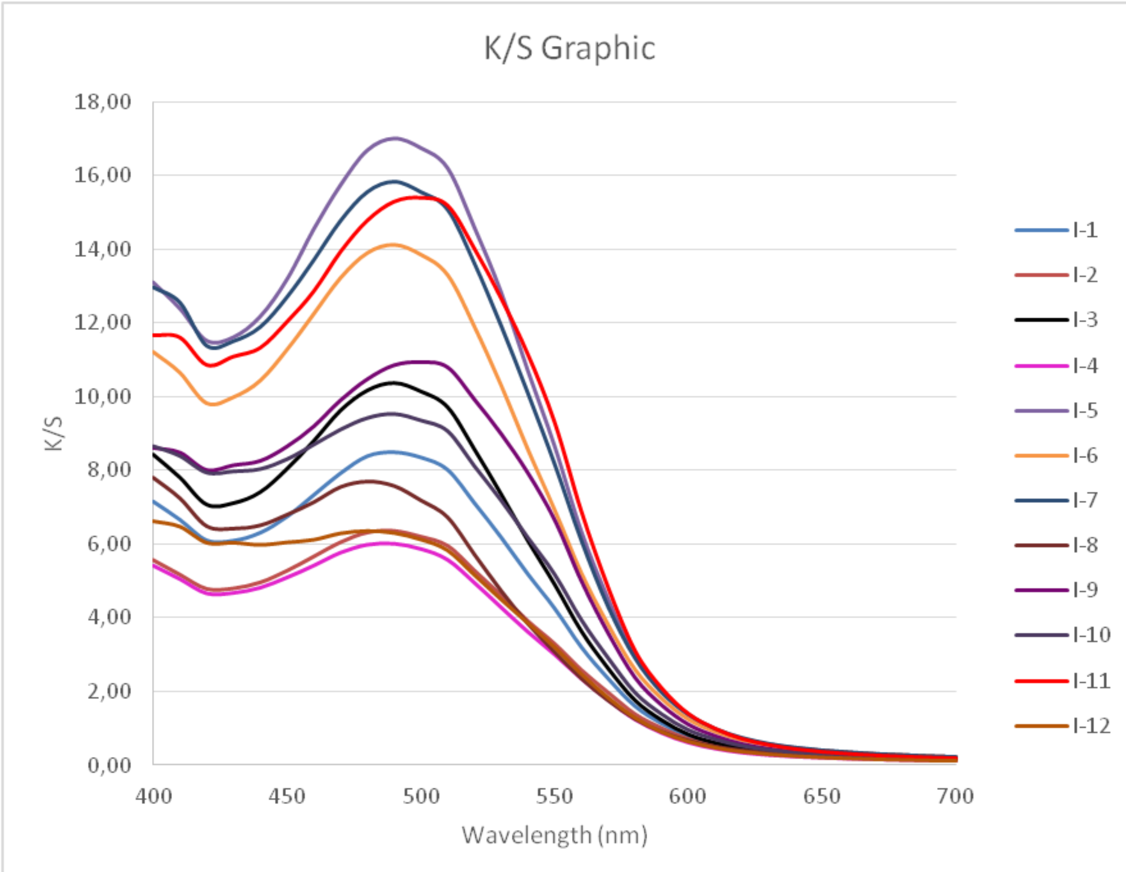


Figure 6:
K/S Graphic of samples

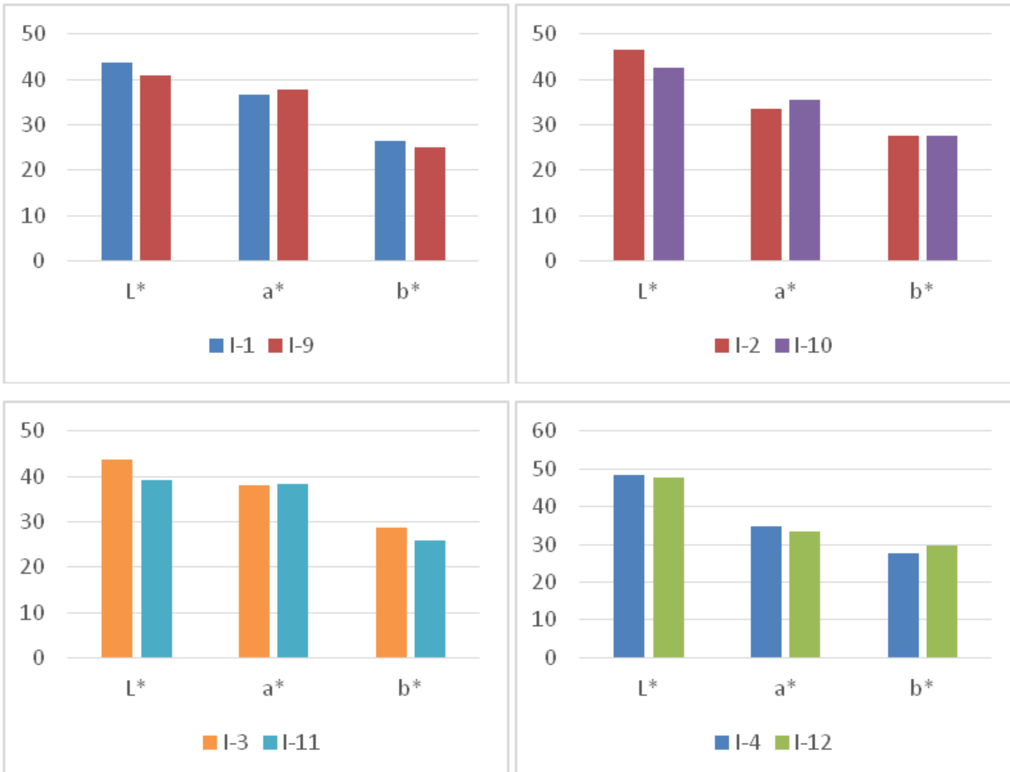


Figure 7:
Effect of ethanol use on color.

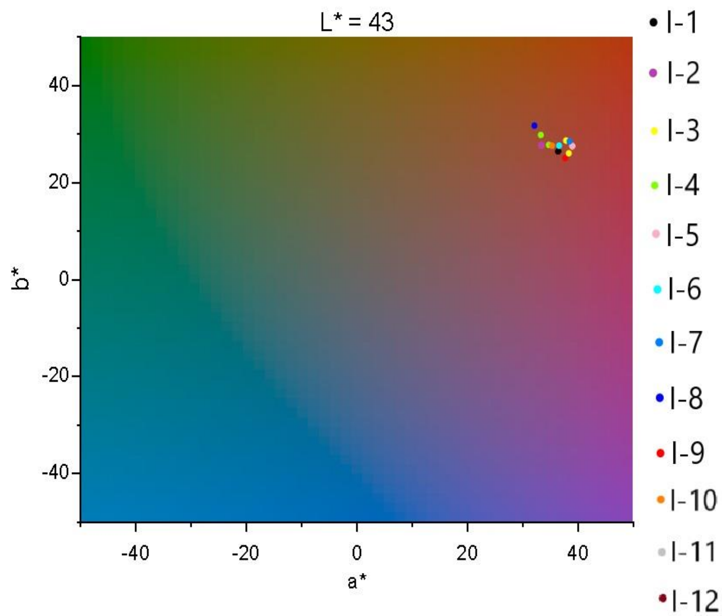


Figure 8:
Positions of the samples in planes a and b* (The L* value is obtained based on the average of samples).*

3.3. Fastness Results

The evaluation of washing fastness values is provided in Table 4. When comparing the washing fastness, it is observed that all values are 4 or higher. It is also observed that the most heavily soiled fiber type is polyamide.

The lightfastness values are given in Table 4. When examining the obtained results, it can be concluded that values of 4 and above indicate good light resistance of this dye in silk dyeing.

Table 4. Washing Fastness Scale Values

Sample Code	Washing Fastness Multifiber Fabric						Light Fastness
	Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate	
I-1	4/5	5	5	4/5	5	5	4/5
I-2	5	5	5	4	4	4/5	4
I-3	5	5	5	4	4	4/5	4
I-4	4/5	5	5	4	4/5	4/5	4
I-5	5	5	5	4	4/5	4/5	4
I-6	4/5	5	5	4	4/5	4/5	4/5
I-7	4/5	5	5	4	4/5	4/5	4/5
I-8	5	5	5	4	5	4/5	4
I-9	5	5	5	4/5	4/5	4/5	4/5

I-10	5	5	5	4/5	4/5	4/5	4/5
I-11	5	5	5	4/5	4/5	4/5	4
I-12	5	5	5	4/5	4/5	4/5	4

4. CONCLUSION

In this study, 100% silk fabrics were dyed with madder (*Rubia Tinctorum* L.) that harvested in Edirne/Havsa. The numerical values of the sample colors have been measured and compared. Lighter colors were obtained as a result of using alum mordant during the dyeing of pre-mordanted silk fabrics. Therefore, it can be said that there is no need to give mordanting chemicals again to pre-mordanted fabrics during the dyeing process. It has been observed that the colors darken as the concentration of the dye increases. The use of TKY has darkened the color, but since the values are low, it can be ignored. It has been observed that the use of ethanol darkens the color. The use of ethanol, which is used as a solvent in extract preparation, together with water in silk dyeing, can be recommended based on the study results. It has been observed that the washing and light fastness values of all samples are within the desired range.

When HPLC analyses were examined, the presence of alizarin was determined to be the highest in the madder. It was followed by munjistin, rubiadin, and purpurin, respectively.

CONFLICT OF INTEREST

The author acknowledges that there is no known conflict of interest or common interest with any institution/organization or person.

AUTHOR CONTRIBUTION

İsmail YÜCE and Nilgün BECENEN performed the experiments and analyses, analyzed the research data to contribute to the design configurations, and also wrote this paper.

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REFERENCES

1. Akman, O. (2021) Edirne Kırmızısı'nın Trakya Üniversitesi Tarafından Edirne Kent Turizmine Kazandırılması Çalışmaları, Yüksek Lisans Tezi, T.Ü. Sosyal Bilimler Enstitüsü, Edirne.
2. Cosmulescu, S. N., Trandafir, I. and Cornescu, F. (2019) Antioxidant capacity, total phenols, total flavonoids and colour component of cornelian cherry (Cornus mas L.) wild genotypes, Notulae Botanicae Horti Agrobotanici Cluj-Napoca, 47(2), 390-394. doi: 10.15835/nbha47111375
3. De Santis, D. and Moresi, M. (2007) Production of alizarin extracts from Rubia tinctorum and assessment of their dyeing properties, Industrial Crops and Products, 26(2), 151-162.doi: 10.1016/j.indcrop.2007.02.002

4. Derksen, G. C., Niederländer, H. A. and van Beek, T. A. (2002) Analysis of anthraquinones in Rubia tinctorum L. by liquid chromatography coupled with diode-array UV and mass spectrometric detection , Journal of chromatography A, 978(1-2), 119-127. doi: 10.1016/S0021-9673(02)01412-7

5. Derksen, G. C., van Beek, T. A., de Groot, Æ. and Capelle, A. (1998) High-performance liquid chromatographic method for the analysis of anthraquinone glycosides and aglycones in madder root (Rubia tinctorum L.), Journal of Chromatography A, 816(2), 277-281. doi: 10.1016/S0021-9673(98)00492-0

6. Ford, L., Rayner, C. M. and Blackburn, R. S. (2015) Isolation and extraction of ruberythric acid from Rubia tinctorum L. and crystal structure elucidation , Phytochemistry, 117, 168-173. doi: 10.1016/j.phytochem.2015.06.015

7. Karapanagiotis, I., Abdel-Kareem, O., Kamaterou, P. and Mantzouris, D. (2021) Identification of dyes in coptic textiles from the museum of faculty of archaeology, cairo university. Heritage, 4(4), 3147-3156. doi: 10.3390/heritage4040176

8. Karapanagiotis, I., and Karadag, R. (2015) Dyes in post-byzantine and ottoman textiles: a comparative HPLC study, Mediterranean Archaeology and Archaeometry, 15(1), 177-189. doi: 10.5281/zenodo.15052

9. Kasiri, M. B., and Safapour, S. (2015) Exploring and exploiting plants extracts as the natural dyes/antimicrobials in textiles processing , Prog. Color Colorants Coat., 8 , 87-114. doi: 10.30509/PCCC.2015.75856

10. Marhoume, F. Z., Aboufatima, R., Zaid, Y., Limami, Y., Duval, R. E., Laadraoui, J., ... and Bagri, A. (2021) Antioxidant and polyphenol-rich ethanolic extract of rubia tinctorum L. prevents urolithiasis in an ethylene glycol experimental model in rats, Molecules, 26(4), 1005.doi: 10.3390/molecules26041005

11. Özer, L. M., Karadağ, R. and Torgan, E. (2016) Investigation of the Effect of Turkey Red Oil on Colour, Fastness Properties and HPLC-DAD Analysis of Silk Fabrics Dyed with Madder (Rubia Tinctorium L.) and Gall Oak, Tekstil ve Mühendis, 23(103), 197-204. doi:10.7216/1300759920162310305

12. Pereira, R. F., Silva, M. M. and de Zea Bermudez, V. (2015) Bombyx mori silk fibers: an outstanding family of materials, Macromolecular materials and engineering, 300(12), 1171-1198.doi: 10.1002/mame.201400276

13. Singh, K., Kumar, P. and Singh, N. V. (2020) Natural dyes: an emerging ecofriendly solution for textile industries, Poll Res, 39(2), S87-S94.

14. TS EN ISO 105-B02, (2013). Textiles — Tests for colour fastness — Part B02: Colour fastness to artificial light: Xenon arc fading lamp test, Turkish Standards Institute, Ankara.

15. TS- EN-ISO105 C06, (2010). Textiles — Tests for colour fastness — Part C06: Colour fastness to domestic and commercial laundering, Turkish Standards Institute, Ankara.

16. Yang, Y. Q. and Li, S. (1993) Silk fabric non-formaldehyde crease-resistant finishing using citric acid, Journal of the Textile Institute, 84(4), 638-644. doi: 10.1080/00405009308658995

17. Yılmaz Şahinbaşkan, B., Karadag, R. and Torgan, E. (2018) Dyeing of silk fabric with natural dyes extracted from cochineal (Dactylopius coccus Costa) and gall oak (Quercus infectoria Olivier), Journal of Natural Fibers, 15(4), 559-574. doi: 10.1080/15440478.2017.1349708