Investigation on colour, fastness properties and HPLC-DAD analysis of silk fibers dyed with madder (Rubia tinctorium) and walloon oak (Quercus ithaburensis)

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Abstract

Silk fabric samples were dyed according to the various procedures using madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) extracts. The colour coordinates, K/S, as well as wash, light, rub and perspiration fastness values were determined. A reversed phase high performance liquid chromatography (RP-HPLC) with diode-array detection (DAD) was utilized for the identification of the components of dyes present in the dyed fabrics and in the plant extracts.

Introduction

The roots of madder have been used for dyeing textile fibers such as wool, silk, and cotton in many parts of the world since ancient times [1-7]. Madder (*Rubia tinctorium* L.) plant contains alizarin, pseudopurpurin, munjistin and as many as 15 other anthraquinone as effective dyes [8]. The red anthraquinone dyes present in madder are probably the most widespread with any other red plant dyes since antiquity [2-5]. Madder is a dye found in the roots of various plants of the Rubiaceae family: *Rubia tinctorum, R. peregrina, R. cordifolia, R. munjista, R. davisiana, R. tenifolia* and others. Plants of this family grow in South America and Europe [4]. It was found in archaeological materials as a colouring material [6]. Many historical red dyes are anthraquinones [9]. Walloon oak (*Quercus ithaburensis* Decaisne) is a tree growing to 15-20 m in open forests in Turkey and Greece. The acorn caps of walloon oak contain 25-35 % tannin. The hydrolyzable tannin *i.e.*, ellagic acid was found in the bark of walloon oak [10]. The several anthraquinone derivatives used in dyeing fibers exhibited various biological activities, such as anti-oxidant, anti-microbial, anti-fungal, cytotoxic, larvicidal, anti-viral as well as the genotoxic activities [11]. Several analytical techniques for the identification of natural dyes present in textiles have been applied such as high performance liquid chromatography [12], UV-visible spectrophotometry, thin layer chromatography [8,13], raman spectroscopy [14], microspectrofluorimetry [15] and gas chromatography/mass spectrometry [16]. HPLC has become an important method for identification of natural dyes present in historical textiles, art objects, *etc*. [17,18].

In this study HPLC-DAD method was used for the seperation and identification of anthraquinone and tannin components present in silk fabrics dyed with madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne). The dyed samples, with or without premordanting (reference sample), were studied colorimetrically and their colour coordinates L*, a*, b*, c*, h* and K/S values are reported. Their fastness properties (wash, light, rub and perspiration), the effect of the mordant, fibre structure on the colour, dye adsorption and fastness properties were also studied.

Experimental

Materials

100 % silk, sateen weave S 4/1 (3), ready for dyeing fabrics were used in this study. The sateen weave used a 4/1 weaving ratio, floating each weft thread under 4 warp threads, then over one thread and the rotation used was 3. The warp density per cm of the fabric was 160 and the weft density per cm was 60. The weight of the fabric was 74 g/m^2.

Dye plants and chemicals

All reagents were analytically graded, unless stated otherwise.Madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) were obtained from Turkish Cultural Foundation, the Research and Development Laboratory for Natural Dyes.The following standard dyes have been used as references: alizarin from Carl Roth (Karlsrube, Germany), xanthopurpurin, rubiadin and purpurin that were synthesized by the University of Jordan.Alum ($KAl(SO_4)_2.12H_2O$), hydrochloric acid, and methyl alcoholwere obtained from Merck (Darmstadt, Germany).

Procedures

Mordanting procedure

40.71 g alum [$KAl(SO_4)_2.12H_2O$] was used for mordanting 116.31 g of silk fabric samples. Mordanting was realized with mordant in proportion as 35 % of textile quantity. The alum mordants were dissolved in warm ultra pure water (silk fabric quantity/ water quantity ; 1/100). Then, the silk fabrics were wetted by ultra pure water and added to the mordant bath at 60ºC. The mordant bath was heated to 90ºC and kept at 75ºC for 1 h.The silk fabrics were mordanted in the mordant bath for 72 h at room temperature.

Extraction

84.5 g of dried and ground madder roots with pochette and 34.1 g of ground walloon oak acorn cupswere transferred to two apart beakers.5000 mL ultra pure water in the case of madder and 2000 mL ultra pure water for walloon oak were then added. Separetly, the extracts of madder roots and walloon oak were heated to 100 ºC. During the heating, the extracts were mixed with a magnet mixer. The temperature of the extracts were decreased to 70 ºC and the extracts were kept at 70 ºC for 1 h. The madder and walloon oak extracts were then obtained for dyeings.

Dyeing procedures

Dyeing with Walloon oak (*Quercus ithaburensis* Decaisne):The fabrics were separetely dyed with 50 % (80 mL), 40 % (65 mL), 30 % (50 mL), 20 % (30 mL) and 10 % (15 mL) walloon oak (*Quercus ithaburensis* Decaisne) extract at 60ºC for 1 h. To be taken at 325 mL to the total dye bath volume, the extracts were added with ultra pure water. After dyeing the dyed silk fabrics were taken out from the dye bathes, washed using ultra pure water and dried at room temperature.

Dyeing with Madder (*Rubia tinctorium* L.*)*: The fabrics were dyed by ultra pure water (162 mL) with 100 % (163 mL) madder (*Rubia tinctorium* L.) extract at 60ºC for 1 h. The dyed fabrics were, then, taken out from the dye bathes, washed with ultra pure water and dried at room temperature.

Eight different dyeing procedure combinations with or without walloon oak and madder were investigated for this experimental study.

Procedure I

The mordanted silk fabrics were dyed with different concentration of the mixture of walloon oak and madder extracts in the same dye bath. The volumes for dyed silk fabrics with walloon oak and madderat the same baths are given in Table 1.

Procedure II

The mordanted silk fabrics were dyed with 100 % madder extract. The dyed and washed fabrics were then dyed again with different concentration of walloon oak extracts. The volumes of dyed silk fabrics with madder and walloon oak dye bathes are given in Table 1.

Procedure III

The mordanted silk fabrics were separetely dyed with different concentration (50-10 %) of walloon oak extracts. The dyed fabrics in walloon oak dye bathes were dyed again with different concentration of madder extracts (100-20 %). The volumes for dyed silk fabrics with walloon oak and madder dye bathes are given in Table 1.

Procedure IV

The mordanted silk fabrics were separetely dyed with different concentration of walloon oak extracts. The volumes for dyed silk fabrics with walloon oak and madder dye bathes are summarized in Table 1, separately.

Procedure V

The unmordanted silk fabrics were separetely dyed with different concentration of walloon oak extracts. The dyed fabrics with walloon oak were, then, mordanted using 35 % alum [$KAl(SO_4)_2.12H_2O$] mordant solution in 325 mL ultra pure water. The dyed fabrics were dried at room temperature. The wet mordanted fabrics were dyed with madder extracts. The volumes for dyed silk fabrics with walloon oak, mordanted by alum and dyed in madder dye bathes are given in Table 1.

Procedure VI

The unmordanted silk fabrics were dyed with walloon oak extracts as explained in procedure III. The dyed fabrics were dyed again using 100 % madder extracts. The volumes for dyed silk fabrics with walloon oak and madder dye bathes are given in Table 1.

Procedure VII

The wet unmordanted silk fabrics were separetely dyed with walloon oak extracts as explained in procedure V. The volumes for dyed unmordanted silk fabrics with walloon oak are given in Table 1.

Procedure VIII

The mordanted silk fabrics were separetely dyed with different concentration of madder extracts. The volumes for dyed mordanted silk fabrics with madder are given in Table 1.

Colour measurements

The colour measurements were performed using Datacolor SF 600 plus spectrophotometer coupled to a PC under D65/10° illuminant with a specular component included. The untreated fabric was taken as standard. The colour differences, according to the CIELab (1976) equation, were obtained from the colour measuring software. The average of the measurements of the samples was recorded as colour yield (K/S) and colour differences (ΔE*).

The Kubelka-Munk equation relates the absorption function of the substrate (K), the scattering function of the substrate (S) and the reflectance (R) in visible spectrum (400-700 nm) according to equation (1) given below.

$$K/S = \frac{(1-R)^2}{2R}$$ (Equation 1) [22].

On the other hand, the colour differences is expressed as ΔE* and is calculated by the following equation (2).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$ (Equation 2)

where ΔE* is the CIELab colour difference between batch and standard. Here ΔL*, Δa*, Δb* and hence ΔE* are in commensurate units. ΔL* denotes the difference between lightness (where L*=100) and darkness (where L*=0), Δa* the difference between green (-a*) and red (+a*) and Δb* the difference between yellow (+b*) and blue (-b*) [22].

Fastness Determination

Wash, light, rub and perspiration fastness properties were carried out respectively in accordance with the methods described in ISO 105-C06 (A1S), ISO 105-B02, ISO 105-X12, and ISO 105-E04 standards. The dyed samples were exposed to the light for 90 h by xenon arch lamp (250 watt).

HPLC method

Chromatographic experiments were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including a G1329A ALS autosampler, a G1315A diode-array detector. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 255 nm. A G1322A vacuum degasser and a G1316A thermostatted column compartment were used. The data were analyzed using Agilent Chemstation. A Nova-Pak C_{18} analytical column (3,9 x 150 mm, 4 µm, Part No WAT 086344, Waters) protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30°C. The HPLC gradient elution was performed using the method of (Halpine, 1996 and Karapanagiotis et al., 2005). Chromatographic separations of the hydrolysed samples were performed using a gradient elution program that utilizes two solvents: solvent A: H_2O - 0.1% TFA (trifluoroacetic acid) and solvent B: CH_3CN (acetonitrile) - 0.1 % TFA. The flow rate was 0.5 mL/min and the elution program was as described earlier [10,19-21].

Extraction procedure for HPLC analysis

The extraction from the dye plants and the dyed silk fabrics was performed by using the previously described method [19-24].

The dyed silk fabrics (4.0-6.7 mg) and dye plants (11.3 mg for madder and 2.3 mg for walloon oak) were hydrolysed by using H_2O:MeOH:37 % HCl (1:1:2; v/v/v; 400 µl) in conical glass tubes for precisely 8 min in a water-bath at 100ºC to extract organic dyes. After rapid cooling under running cold water, the solution was evaporated just to dryness in a water-bath at 50-65ºC under a gentle stream of nitrogen. The dry residues were dissolved in 400 µl of the mixture of MeOH: H_2O (2:1; v/v). 10 or 35 µl of the supernatant and were injected into the HPLC apparatus.

Results and Discussion

HPLC analysis

The dye compositions were identified based on literatures, the chromatograms, and the absorption spectra acquired with the standard reference compounds [10,11,21,25]. One of the metal salts i.e. the aluminium (III) salt was used as mordant in traditional dyeing process with natural dyes, consisting of tannnin and anthraquinones. The sample preparation for the extraction of dye components from the dyed silk fibres is based on the commonly used hydrolysis procedure with hydrochloric acid. For the extracts at this treatment is necessary to isolate the organic dye from its mordant metal. Chromatographic and spectral characteristics of the investigated dyes in this study are given in Table 2.

In the acid hydrolysed madder (*Rubia tinctorium* L.), alizarin, rubiadin, and purpurin are observed together with relatively minor amounts of munjistin by HPLC-DAD (monitored at 255). The peak of 30.1 min retention time was determined, however could not be identifed and therefore, are not discussed.

The gallic acid and ellagic acid identified in the acid hydrolysed walloon oak (*Quercus ithaburensis* Decaisne) acorn cups are identified. The peak of 16.8 min retention time is determined. Probably, this unidentifed peak belongs to an ellagic acid derivative.

Natural dyes identified in silk fabrics dyed according to the receipts of different procedure are presented in Table 3. Ellagic acid, alizarin, and purpurin are determined in the acid hydrolysed silk extracts.

Effects of different dyeing procedures on the CIEL*a*b* values

Table 4 shows the maximum K/S (colour yield) values of the all dyed silk fabrics by the use of different dyeing processes. The K/S value of a dye is related to the concentration of the dye on the textile material, i.e. the importance of the value is a direct measure of dye depth shade. Therefore, from the Table 2, it can be said that in general the highest K/S values were obtained from groups I, II and III, the lowest colour yield value was obtained from group VII. CIE L*, a*, b*, C* and h values for untreated and dyed silk fabrics are given in Table 4. Hue angle (h) are showed that, the fabrics dyeing by procedure IV and VII have yellowish and light colour. Other dyed fabrics have reddish and dark colour.

ΔE* values (total colour difference) are given in Table 4 and higher in most procedures. This differences showed that silk fabric samples can be dyed with all procedures by using madder and walloon oak.

Fastness Properties

The wash, light, rub and perspiration fastnesses of the dyed samples are given in Table 5. Colour change gradings in general had very poor fastness to wash (1). Also for the 1., 9., 34. and 35. samples had quite good colour change gradings (4). The wash fastness results for the staining on nylon and wool showed that dyeing with madder and walloon oak together in general decreased wash fastness. The samples dyeing with other procedures also gave an improvement in wash fastness.

Unmortanted group VII (31-35) had very poor fastness to light (2), whereas mordanted group IV (16-20) had moderate fastness (3). The light fastness test results of the dyed silk fabric samples which are mordanted group I and II are quite better than the other groups.

The rub fastness results for the dyed fabrics showed that dyeing silk fabrics with madder or walloon oak in general obtained quite good rub fastness (4-5). The wet rub fastness of group V was only slightly better (3-4).

The perspiration fastness test results of samples had the quite better (4) for the mordanted group IV than the other samples. Group I, II and VI had very poor (1-2) fastness to perspiration.

Conclusion

In this study, the various dyeing procedures using madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) dye plants were performed for the silk fabrics. The identification of the dyes from the dye plants and the dyed silk fabrics were achieved using RP-HPLC with DAD. The HPLC method allowed qualitative determination of the natural dyes in the dyed fabrics and extracts prepared.

100% silk fabric can be dyed with madder (*Rubia tinctorium* L.) and Walloon oak (*Quercus ithaburensis* Decaisne) using the eight different procedures. The silk fabrics dyed using procedure IV and VII have light yellowish colour.

In overall results, use of madder and walloon oak together in the same dye bath in general appears to improve wash fastness. The light and wet/dry rub fastness test results are quite good. In contrast, perspiration fastness values were in most cases, except group IV, slightly decreased.

Finally, we believe that dyeing protein fibers with natural dyes (madder and walloon oak) can be an important advantage for the enviromental processes.

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Table 1. Dyeing properties for silk fabrics dyed according to the different procedures.

Procedure	Sample No	Mordant (%	Walloon oak (%)	Madder (%)	Liquor ratio	Temperature (ºC)	Time (min)
I	1	35	50	100	440:1	60	60
	2	35	40	100	440:1	60	60
	3	35	30	100	440:1	60	60
	4	35	20	100	440:1	60	60
	5	35	10	100	440:1	60	60
II	6	35	50	100	440:1	60	60
	7	35	40	100	440:1	60	60
	8	35	30	100	440:1	60	60
	9	35	20	100	440:1	60	60
	10	35	10	100	440:1	60	60
III	11	35	50	100	440:1	60	60
	12	35	40	80	440:1	60	60
	13	35	30	60	440:1	60	60
	14	35	20	40	440:1	60	60
	15	35	10	20	440:1	60	60
IV	16	35	50	-	440:1	60	60
	17	35	40	-	440:1	60	60
	18	35	30	-	440:1	60	60
	19	35	20	-	440:1	60	60
	20	35	10	-	440:1	60	60
V	21	35	50	100	440:1	60	60
	22	35	40	100	440:1	60	60
	23	35	30	100	440:1	60	60
	24	35	20	100	440:1	60	60
	25	35	10	100	440:1	60	60
VI	26	-	50	100	440:1	60	60
	27	-	40	100	440:1	60	60
	28	-	30	100	440:1	60	60
	29	-	20	100	440:1	60	60
	30	-	10	100	440:1	60	60
VII	31	-	50	-	440:1	60	60
	32	-	40	-	440:1	60	60
	33	-	30	-	440:1	60	60
	34	-	20	-	440:1	60	60
	35	-	10	-	440:1	60	60
VIII	36	35	50	100	440:1	60	60
	37	35	40	80	440:1	60	60
	38	35	30	60	440:1	60	60
	39	35	20	40	440:1	60	60
	40	35	10	20	440:1	60	60

Table 2. Chromatographic and spectral characteristics of the investigated reference dyes.

Dye (Standard)	Retention time in the given protocol (min)	UV-VIS data
Gallic acid	4.4	215, 271
Ellagic acid	17.5	251, 307, 367
Munjistin	28.2	245, 274, 336, 403
Alizarin	28.3	249, 279, 331, 433
Purpurin	30.2	255, 295, 481, 520
Rubiadin	31.6	243, 279, 331, 413

Table 3. The dyes detected in the acid hydrolysed silk extracts.

Sample No	Dyes detected
	Silk (Acid hydrolysed extract)
1	Ellagic acid, alizarin, purpurin
5	Ellagic acid, alizarin, purpurin
6	Ellagic acid, alizarin, purpurin
10	Ellagic acid, alizarin, purpurin
11	Ellagic acid, alizarin, purpurin
15	Ellagic acid, alizarin, purpurin
16	Ellagic acid
20	Ellagic acid
21	Ellagic acid, alizarin, purpurin
25	Ellagic acid, alizarin, purpurin
26	Ellagic acid, alizarin, purpurin
30	Alizarin, purpurin
31	Ellagic acid
35	Ellagic acid
36	Alizarin, purpurin
40	Alizarin, purpurin

Table 4. Effect of different dyeing procedures on the CIE L*a*b* colour coordinates, colour differences and maximum K/S values of dyed silk fabrics with madder and walloon oak.

Samples	**L***	**a***	**b***	**C***	**H**	ΔE* [a]	**K/S (λ_{max}=400)**
Untreated	93.53	0.41	4.03	4.05	84.23	-	0.06
1	57.60	19.72	31.06	39.79	57.59	48.93	9.20
2	57.40	21.05	31.09	37.55	55.90	49.63	8.77
3	57.56	22.16	30.68	37.84	54.15	49.77	8.01
4	57.87	24.63	30.29	39.04	50.88	50.48	6.71
5	56.81	28.26	28.66	40.25	45.40	52.25	5.52
6	56.11	16.11	30.61	34.59	62.25	48.51	9.95
7	55.80	16.28	30.52	34.60	61.92	48.76	9.90
8	56.08	16.84	30.11	34.36	61.22	48.50	8.97
9	56.69	17.90	29.76	34.73	58.97	48.22	7.77
10	57.40	19.79	28.48	34.68	55.20	47.74	6.00
11	58.49	15.08	30.06	33.63	63.35	46.05	9.65
12	59.54	14.49	29.44	32.81	63.79	44.71	8.78
13	62.04	12.15	28.78	31.36	66.60	41.74	7.69
14	64.64	11.31	27.40	29.64	67.58	38.72	6.01
15	69.53	9.06	24.59	26.20	69.78	32.76	3.59
16	67.80	1.13	30.05	30.07	87.86	36.60	9.01
17	68.41	1.04	29.67	29.69	87.99	35.90	8.43
18	69.47	0.80	29.32	29.34	88.43	34.91	7.60
19	71.15	1.05	27.28	27.30	87.80	32.28	5.41
20	73.66	1.31	25.14	25.17	86.99	29.00	3.62
21	58.26	14.21	27.61	31.05	62.76	44.61	6.84
22	57.62	15.81	26.59	30.93	59.26	45.12	6.41
23	56.93	18.34	25.56	31.46	54.35	46.09	5.78
24	56.79	21.85	25.99	33.96	49.95	47.87	5.03
25	58.66	23.79	26.40	35.54	47.98	47.57	3.71
26	63.09	16.28	32.77	36.59	63.58	44.77	4.59
27	63.11	16.92	33.31	37.36	63.08	45.34	4.50
28	63.93	17.41	32.86	37.19	62.09	44.68	3.99
29	64.85	19.50	33.04	38.36	59.45	45.04	3.53
30	67.30	23.09	32.60	39.95	54.86	44.93	2.69
31	69.67	3.69	20.53	20.85	79.80	29.19	3.19
32	69.82	3.75	20.40	20.74	79.59	29.01	3.02
33	71.01	3.52	19.35	19.67	79.69	27.41	2.51
34	75.22	2.81	17.43	17.66	80.83	22.82	1.58
35	81.88	1.83	13.69	13.81	82.38	15.20	0.72
36	56.46	29.27	27.66	40.27	43.38	52.59	3.74
37	59.36	26.90	25.79	37.27	43.80	48.40	2.90
38	61.23	25.27	24.07	34.90	43.61	45.42	2.44
39	64.53	23.40	21.76	31.95	42.92	41.04	1.82
40	69.99	20.75	18.14	27.56	41.17	34.16	1.08

([a]The untreated fabric was taken as "standard".)

Table 5. Fastness results of the dyed silk fabrics.

Samples	**Wash Fastness***			**Light Fastness**	**Rub Fastness**		**Perspiration Fastness***			
	CC	**SN**	**SW**		**Dry**	**Wet**	**Alkaline**		**Acid**	
							SN	**SW**	**SN**	**SW**
1	4	3	3	5	4-5	4	1	1	1	1
2	3	3	4	5	4-5	4-5	1	1	1	1
3	2	3	3	5	4-5	4	1	1	1	1
4	1	3	3	6	4-5	4	1	2	1	1
5	1	3	3	7	5	4	1	2	1	1
6	2	3	3	7	5	4	1	1	1	1
7	2	3	3	4	5	4	1	1	1	1
8	3	4	4	5	5	4-5	1	1	1	1
9	4	4	4	5	4-5	4	1	1	1	2
10	1	4	4	7	4-5	4-5	1	2	1	2
11	2	4	4	6	4-5	4	1	2	1	2
12	1	4	4	6	4-5	4	1	2	1	2
13	1	4	4	5	4-5	4	1	2	1	3
14	2	4	4	4	4-5	4-5	1	2	1	3
15	2	4	3	5	4	4	3	4	3	4
16	1	4	4	3	4-5	4-5	3	4	4	4
17	1	4	3-4	3	4	4	3	4	4	4
18	1	4	4	3	4-5	4	4	4	4	4
19	1	4	3	3	4	4	3	4	4	4
20	1	4	4	3	4-5	4	4	4	4	4
21	3	4	4	5	4-5	3-4	1	3	1	2
22	1	4	4	6	4-5	3-4	2	3-4	1	2
23	1	4	4	6	4-5	3-4	3	3-4	1	2
24	1	4	4	5	4-5	4	3	3-4	1	2
25	1	4	2	4	4-5	4	3	3-4	1	1
26	1	3	1	5	5	4	1	1	1	1
27	1	3	1	6	5	4-5	1	1	1	1
28	1	4	3	5	5	4	1	1	1	1
29	1	3-4	2	6	5	5	1	1	1	1
30	3	4	4	2	5	5	1	1	1	1
31	3	4	3-4	2	5	4-5	1	2	4	4
32	2-3	4	4	2	5	4-5	2	2	4	3-4
33	3	4	4	2	5	4-5	2	2	4	3-4
34	4	4	4	3	5	4-5	3	2	4	4
35	4	4	4	4	5	5	2	3	4	4
36	1	4	4	4	4	4	3	3	1	3
37	1	4	4	4	4-5	4	3	3-4	1	3
38	1	4	4	4	4-5	4	3	3-4	1	3
39	2	4	4	3	4-5	4	3	3-4	1	3
40	2	4	4	3	4-5	4	3	3-4	2	3-4

[*] CC= Colour Change; SN= Staining on Nylon; SW= Staining on Wool.