Study of Textile Materials Behavior at Dyeing with Colored Aqueous Extract Obtained by Boiling Peels, Arils and Seeds of *Punica Granatum*
Spectroscopic, colorimetric and statistic evaluations

VASILICA POPESCU[1], IRINA CRINA ANCA SANDU[2, 3], GABRIEL POPESCU[4*]

[1]Gheorghe Asachi Technical University of Iasi, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Dimitrie Mangeron Blvd., 700050 Iasi, Romania

[2]Munch Museum/Munch Museet, Department of Conservation, Toyengata, 53 0578 Oslo, Norway

[3]Romanian Inventors Forum, 3 Sf. P. Movila St., L11, III/3, 700089, Iasi, Romania

[4]Gheorghe Asachi Technical University of Iasi, Faculty of Mechanical Engineering, 43 Dimitrie Mangeron Blvd., 700050 Iasi, Romania

The extraction of natural pigments from the peels, arils and seeds of Punica granatum was accomplished by boiling them in the presence of water as solvent. Boiled extract/brown solution (CSF brown solution) was used to dye, in the same dyebath, 4 types of textile materials (wool, polyamide, cotton and cellulose acetate) using a pre-mordanting procedure. The nettle extract obtained as decoct was used as mordant. At the end of pre-mordanting stage (15 min), the extract obtained by boiling pomegranate peels, arils and seeds was added with the view to perform the dyeing. One has used 5 volumetric ratios mordant (mL): CSF brown solution (mL): 0:120; 60:60; 30:90, 90:30 and 50:120. Dyeing was performed at 100ºC for 60 min. The effect of textiles dyeing was confirmed by FTIR analysis and color measurements. The parameter % strength SUM was calculated to study especially the mordant influence; was used the comparison of the sample pre-treated with mordant but dyed with CSF brown solution, with the sample dyed with CSF brown solution (without mordant). A statistic analysis was carried out for % strength SUM, computing the values of standard deviations (SD), standard errors of mean (SEM) and the coefficient of variation (CV).

Keywords: peels, arils pomegranate, colorimetry, SUM strength, statistical analysis

In the world, there are over 500 assortments of pomegranates, 50 of which are cultivated to be traded [1]. Each pomegranate assortment is characterized by a certain content of natural dyes and by colors varying from yellow-red to violet. The most encountered natural dyes from pomegranates are: gamma tocopherol (yellow) in arils and anthocyanins in arils with seeds (Cyanidin 3-*O*- glucoside, Cyanidin 3,5-di-*O*-glucoside, Delphinidin 3-*O*-glucoside, Delphinidin 3,5-di-*O*-glucoside, Pelargonidin 3-*O*-glucoside, Pelargonidin 3,5-di-*O*-glucoside) [2-4]. In Pomegranate peel one can find anthocyanidins (Delphinidin with bluish hue) [5-8] and Pelletierine alkaloids (as Pseudopelletierene or N-methyl granatonine-colorless or yellow on exposure) [9-11].

Anthocyanine presence in pomegranate depends on fruits variety and maturity, namely: delphinidin-3, 5-diglucoside prevails before maturation, while cyaniding-3-glucoside and cyaniding-3, 5-diglucoside prevails after maturation [12].

By combining the colors of all pomegranate assortments, one obtains a final brown color after keeping it for a certain period, even at room temperature [13, 14]. The brown color is the result of degradation of monomer anthocyanins and/or polymerization of anthocyanins from pomegranates juice [15]. Anthocyanins stability depends on their chemical nature, processing/stocking temperature, and light, presence of oxygen, enzymes, metal ions, ascorbic acid, hydrogen peroxide, sulfur dioxide, sulfite salts, sugar and pH. Boiling the pomegranate juice just after producing it (by pressing) removes the risk of polyphenols oxidization, because the enzyme which determines the appearance of brown color (native polyphenol oxydase) is no longer formed [2, 16]. This enzyme determines polyphenols conversion to O-quinones during an enzymatic browning process; the reaction between them leads to the degradation of monomer anthocyanins, for which reason this is considered as an indirect degradation [9].

Each pomegranate species contains natural pigments and several condensed tannins; they are found in certain amounts in arils, seeds, rind/peel or mesocarp. The brown color can be the result of the formation of a complex compound (between anthocyanins and condensed tannins) or of anthocyanins degradation. While in alimentation the brown color is disturbing, because it means the diminution of the content of anti-oxidant substances (anthocyanins) beneficial for health, this is no inconvenience in the case of textile dyeing (with this brown solution).

In this work, the CSF brown solution obtained by boiling rinds/peels and arils with seeds was used to dye wool, polyamide, cotton and cellulose acetate samples. Dyeing was accomplished in two stages: pre-mordanting with nettle decoct (15 min) and then adding the CSF brown solution. Dyeing operations were performed at 100ºC (for 60 min) using five volumetric mordant (mL): CSF brown solution (mL) ratios. The effects of textile material dyeing were confirmed by FTIR analysis, color measurements and statistic analysis for the parameter % strength SUM.

Experimental part
Materials and methods

The textile materials were acquired from textile companies from Romania: wool from Carpatex Brasov, and other textiles from Iasitex Iasi.

Solid- liquid extraction: The mixture of pomegranate peels, arils and seeds (50g) with 1000 mL distilled water was boiled for one hour, then storaged for one month, to complete the extraction process.

* email: gpopescu65@yahoo.com

Mordant : CSF brown solution (mL : mL)	Wool code	Polyamide code	Cotton code	Cellulose acetate code
0 : 0	Reference_W	Reference_PA	Reference_C	Reference_CA
0 : 120	0CSF_W	0CSF_PA	0CSF_C	0CSF_CA
60 : 60	1CSF_W	1CSF_PA	1CSF_C	1CSF_CA
30 : 90	2CSF_W	2CSF_PA	2CSF_C	2CSF_CA
90 : 30	3CSF_W	3CSF_PA	3CSF_C	3CSF_CA
50 :120	4CSF_W	4CSF_PA	4CSF_C	4CSF_CA

Textiles dyeing were accomplished in two stages: 1) mordanting with nettle extract for 15 min; 2) dyeing in itself with CSF brown solution obtained by boiling pomegranate peels, arils and seeds. The experimental protocol is presented in table 1, where are indicated the five volumetric ratios: mordant: CFS brown solution used for dyeing. In the dyeing recipient were introduced each time all the 4 types of textile materials, cut at the size of 10x10 cm. Each dyeing operation was repeated ten times, to allow a statistical analysis of the color strength in the presence of mordant, by appreciating the coefficient of variation of the parameter % strength SUM. The dyeing was performed on Mathiers Policolor machine at 100ºC for 60 min. Intense washing in hot and finally cold water followed the dyeing.

Methods of analysis

FTIR – analysis was performed on a Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan). The spectra registration was realized with 250 scans in the 4000–600 cm^{-1} range. The overlapping spectra were performed using Jascow32 software.

Color measurements were measured on a Datacolor Spectrophotometer Sprectroflash SF300. The following colorimetric measurements were performed: colour strength (K/S), CIE L*a*b* measurements (L*, a*, b*, C*, h*) and CIE L*a*b* color differences (ΔE*, ΔL*, ΔC*, Δa*, Äb* and Äh*). The significances of the color measurements [17-30] are as follow: L* and ΔL* are the lightness / luminosity and difference in lightness, respective; a* and Δa* indicate the red-green coordinate and the differences on the red-green coordinate respective; b* and Δb* indicate the blue-yellow coordinate and the differences on the blue-yellow coordinate; C* and ΔC* are the saturation of color and the saturation difference, respectively; h* and Δh* are the hue and the difference is the hue of color; ΔE* = the total differences of color.

Statistical analysis of the % (color) Strength SUM of the dyed samples was used to test, specially, the influence of the mordant presence on the dyeing capacity of samples. The % Strength SUM was tested according to DIN55986 method and represents an apparent strength being calculated as the ratio of (K/S) data between sample and reference at all visual wavelength (400-700 nm); it is expressed in %. The selection of different illuminant observer condition has no influence on the result [26].

The relationship for computation of % strength SUM is given by eq. 1

$$\% \quad Strength \quad SUM \quad = 100 \quad \times \quad \frac{\sum_{400}^{700}\left(\frac{K}{S}\right)_{sample}}{\sum_{400}^{700}\left(\frac{K}{S}\right)_{reference}} \quad (1)$$

where K/S represents the color strength calculated with Kubelka-Munk equation.

If the percent of color strength is higher than 100, then the sample is stronger in color than the reference sample [26].

The power of coloration acquired by the dyed samples was appreciated by percent color strengths (K/S), computated for 10 dyed samples realized in the same conditions, for each material type. The standard deviation SD, the standard error of the mean (SEM) and the coefficient of variation (CV), of the set of distinctive statistic data {(% Strength SUM)$_1$, (% Strength SUM)$_2$, …(% Strength SUM)$_{10}$} were calculated with a MATLAB software [31, 32] using equations similar to those in previous articles [13, 14].

Results and discussions
FTIR spectra

FTIR analysis of the untreated wool was performed in our previous work [14]. By treating with CSF brown solution obtained by boiling rinds/peels and arils with seeds of Punica granatum, one could notice increases of peaks height: 3366cm^{-1}, 1655 cm^{-1}, 1050 cm^{-1} and 621 cm^{-1} (fig. 1a). These increases are due to CSF brown solution and less to mordant, as follows from figure 1.b. The presence of several functional groups of OH type in the natural pigments (anthocyanins and anthocyanidins) [7, 33] existing in CSF brown solution justifies the increase of the specified peaks height.

The spectra 2 and 3 have similar shapes; yet, the FTIR spectrum generated by 0CSF has higher peaks then the spectrum generated by 1CSF. This leads to the idea that the volumetric ratio mordant: CSF brown solution plays an important part in this dyeing operations. At a volumetric ratio 0 mL mordant: 120 mL CSF brown solution, the influence is exerted only by the brown solution, while in 1CSF sample (with the volumetric ratio is 60 mL mordant:
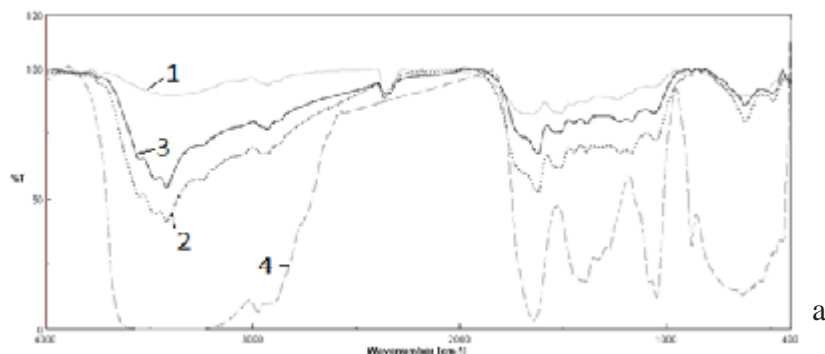

Fig. 1. FTIR spectra for wool: a - untreated wool (1); 0CSF (2), 1CSF (3), CSF brown solution (4); (same codes as in table 1
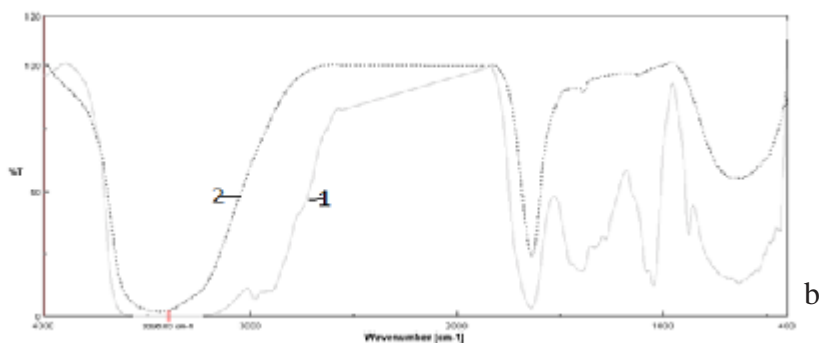
Fig. 1. FTIR spectra for wool: b - CSF brown
solution (1), mordant (2)

b

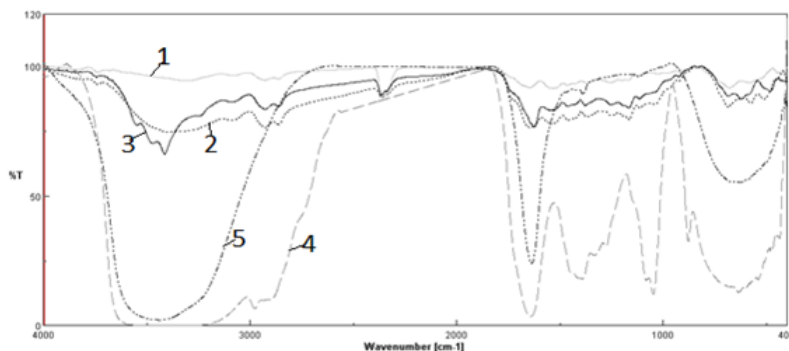| Sample code	Mordant : CSF brown solution (mL : mL)	K/S (at 400 nm)	CIE L*a*b* color				
			L*	a*	b*	C*	h*
Reference_W	0 : 0	0.88	80.10	1.24	14.63	14.69	85.16
0CSF_W	0 : 120	27.99	47.27	8.15	34.33	35.28	76.64
1CSF_W	60 : 60	30.69	43.79	7.03	32.03	32.79	77.63
2CSF_W	30 : 90	29.70	44.90	7.60	32.93	33.79	77.01
3CSF_W	90 : 30	30.73	40.23	6.81	28.74	29.54	76.67
4CSF_W	50 : 120	29.80	46.24	7.84	34.43	35.31	77.17

Fig. 2. FTIR spectra for untreated PA (1);
0CSF (2), 1CSF (3), CSF brown solution (4),
mordant (nettle decoct, 5); (same codes as
in table 1)

60 mL CSF brown solution), the decrease of brown solution volume to 60 mL determined the decrease of color strength K/S (table 2).

FTIR analysis of untreated PA was also performed in our previous work [14]. By treating with CSF brown solution obtained by boiling rinds/peels, arils and seeds from Punica granatum, one can notice height increases of some peaks: 3437 cm^{-1}, 1637 cm^{-1}, 1047 cm^{-1} and 635 cm^{-1}, due to the existence of more OH groups attached to the natural pigments (anthocyanins and anthocyanidins) [7, 33] from the CSF brown solution (fig. 2).

In figure 2 one can notice that the spectra 2 and 3 are very similar with respect to shape and peaks height; a significant difference appears around the value of 3437cm^{-1} assigned to mordant effect.

CIE L*a*b* color

The proofs of more intense dyeing for the studied samples (wool, polyamide, cotton and acetate) than for the reference samples are given by the values of color strength (K/S) [34, 35] and the colorimetric measurements: L*, a*, b*, C* and h*. It is known that the parameters K/S and L* change in inverse proportion, i.e. an intense dyeing has big K/S values and small L* values. Accordingly, the wool dyes the most intense, followed by polyamide, cotton and acetate. Tables 2-5 confirm this fact.

For wool (table 2), mordant presence is beneficial, because it leads to the increase of K/S value; this fact results from comparing the behavior of 0CSF_W sample (K/S = 27.99) with 4CSF_W sample (K/S = 29.80). Even a smaller volume of CSF brown solution combined with a very large mordant amount (case 3 CSF, when the ratio mordant : CSF brown solution is 90:30) results in very high

K/S values (30.73); one obtains close values (K/S = 30.69) when using 60 mL mordant and 60 mL CSF brown solution (1CSF_W case).

CIE L*a*b* parameters from table 2 indicate much smaller values of lightness for the samples dyed with CSF brown solution extracted from pomegranates (L* = 40.23÷47.27), as compared to those of the reference sample (L* = 80.10). The values of a* exceeding 1.24 (afferent to reference sample) indicates a redder hue of the dyed samples, as compared to reference; all the b* values are higher than zero and than b*$_{reference sample}$ (14.63) respectively, which indicates more intense yellow hues as compared to reference sample.

Polyamide dyes poorer than wool: the data from table 3 indicate that K/S values are about 3 times smaller, and L* values range between 52.16 and 58.31, therefore are higher than for wool (40.23÷47.27).

Cotton and cellulose acetate samples have smaller values for all the components of CIE L*, a* and b* color. The K/S values and colorimetric measurements performed on cotton and cellulose acetate samples, dyed with solution extracted from pomegranates indicate that natural dyes from pomegranates belong neither to the class of direct dyes (because they do not dye cotton intensely), nor to the class of dispersion dyes (because they do not dye cellulose acetate, intensely) (tables 4 and 5).

CIE L*, a*, b* color differences

All the wool samples dyed with CSF brown solution extracted from pomegranates through boiling are dyed very intensely as compared to the reference sample (abbreviated as reference_W), which resulted in values ΔE* > 38.975 (fig. 3). The highest value for ΔE* was

Sample code	Mordant : CSF brown solution (mL : mL)	K/S (at 400 nm)	CIE L*a*b* color				
			L*	a*	b*	C*	h*
Reference_PA	0 : 0	0.15	87.44	3.78	4.69	6.02	51.14
0CSF_PA	0 : 120	11.30	58.31	11.59	32.40	34.41	70.32
1CSF_PA	60 : 60	11.60	55.49	9.73	32.50	33.92	73.32
2CSF_PA	30 : 90	11.23	57.82	10.17	32.38	33.94	72.56
3CSF_PA	90 : 30	12.27	52.16	9.76	33.31	34.71	73.68
4CSF_PA	50 : 120	10.91	57.67	11.05	33.29	35.07	71.64

Sample code	Mordant : CSF brown solution (mL : mL)	K/S (at 400 nm)	CIE L*a*b* color				
			L*	a*	b*	C*	h*
Reference_C	0 : 0	0.19	89.37	1.34	8.31	8.42	80.82
0CSF_C	0 :120	3.06	73.74	4.61	21.01	21.51	77.62
1CSF_C	60 : 60	2.25	71.91	3.43	18.06	18.39	79.26
2CSF_C	30 : 90	2.04	73.58	3.69	17.97	18.35	78.41
3CSF_C	90 : 3	1.73	71.41	2.39	17.11	17.28	82.06
4CSF_C	50 :120	2.04	74.57	3.89	18.84	19.23	78.34

Sample code	Mordant : CSF brown solution (mL : mL)	K/S (at 400 nm)	CIE L*a*b* color				
			L*	a*	b*	C*	h*
Reference_CA	0 : 0	0.18	89.64	1.15	7.36	7.45	81.10
0CSF_CA	0 : 120	0.72	84.31	0.95	13.07	13.10	85.83
1CSF_CA	60 : 60	0.88	81.67	1.30	14.23	14.29	84.76
2CSF_CA	30 :90	0.80	82.44	0.85	12.87	12.90	86.22
3CSF_CA	90 : 30	1.03	78.94	0.56	16.09	16.10	87.99
4CSF_CA	50 : 120	0.77	83.78	0.93	12.69	12.72	85.79

obtained in the case of the sample 3CSF_W ($\Delta E^* = 42.739$).

The lightness difference ΔL^* is smaller than zero for each dyed wool sample, which indicates more intense dyeing than that of the reference sample (since $\Delta L^* = L^*_{sample} - L^*_{reference}$).

The smallest value for ΔL^* was recorded for the sample 0CSF_W (-32.916), and the highest value was obtained at the sample 3CSF_W (-39.957), which confirms the importance of the role played by mordant in the dyeing process. The values $\Delta L^* < 0$, correlated with the positive values for a* and b* permit to consider the dyed samples as *darker redder yellow.*

All dyed polyamide samples can be characterized as *darker redder yellow* as compared to reference sample (Reference_PA), for the following reasons: 1) they have ΔE^* values much higher than the reference sample, ranging between 40.96 (for 0CSF_PA sample) and 45.823 (for 3CSF_PA sample); 2) they have $\Delta L^* < 0$, ranging between -29.134 (for 0CSF_PA sample) and -35.282 (for 3CSF_PA sample); 3) they have positive values for Δa^* and Δb^*, which indicates that color variation turns to red and respectively yellow; 4) they have values $\Delta h^* > 0$, which indicates that all the samples have more yellow than the reference sample (fig. 4).

For the dyed cotton samples, positive or negative variations of the parameters CIE L*, a* b*color differences respect the same rules as in the case of wool dyeing; cotton samples dyed with CSF brown solution extracted from pomegranate can be characterized as *darker redder yellow* than the reference (fig. 5).

Yet, the values ΔE^*, ΔL^*, Δa^*, Δb^*, ΔC^*, Δh^* are smaller than in the case of wool (fig. 3), such that maximum obtained values were as follows: ΔE^*=20.398 for 0CSF_C sample; ΔL^*= -17.956 for 3CSF_C sample; Δa^*= 3.268 for 0CSF_C sample; Δb^*= 12.697 for 0CSF_C sample; ΔC^*= 13.089 for 0CSF_C; Δh^*= -0.752 for 0CSF_C sample (fig. 5).

Cellulose acetate samples have CIE L*a*b* color differences smaller than the values obtained on the wool, polyamide and cotton samples (fig. 6). Having $\Delta L^*>0$, $\Delta a^*<0$ and $\Delta b^*>0$, all the cellulose acetate samples are considered to be *darker redder yellow* as compared to the reference sample.

Statistical analysis

If the undyed samples would have been regarded as reference samples then the values for % Strength SUM would have been very large (of the thousands).

For an easier interpretation of the results concerning the effects exerted on color by the used volumes of dye solution
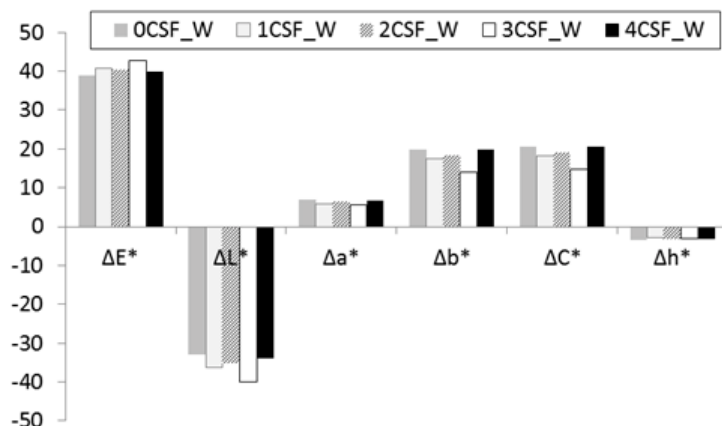

Fig. 3. CIE L*a*b* color difference for wool samples dyed with brown solution extracted by boiling pomegranate peels, arils with seeds

Fig. 4. CIE L*a*b* color difference for polyamide samples dyed with brown solution extracted by boiling pomegranate peels, arils with seeds

Fig. 6. CIE L*a*b* color difference for cellulose acetate samples dyed with brown solution extracted by boiling pomegranate peels, arils with seeds
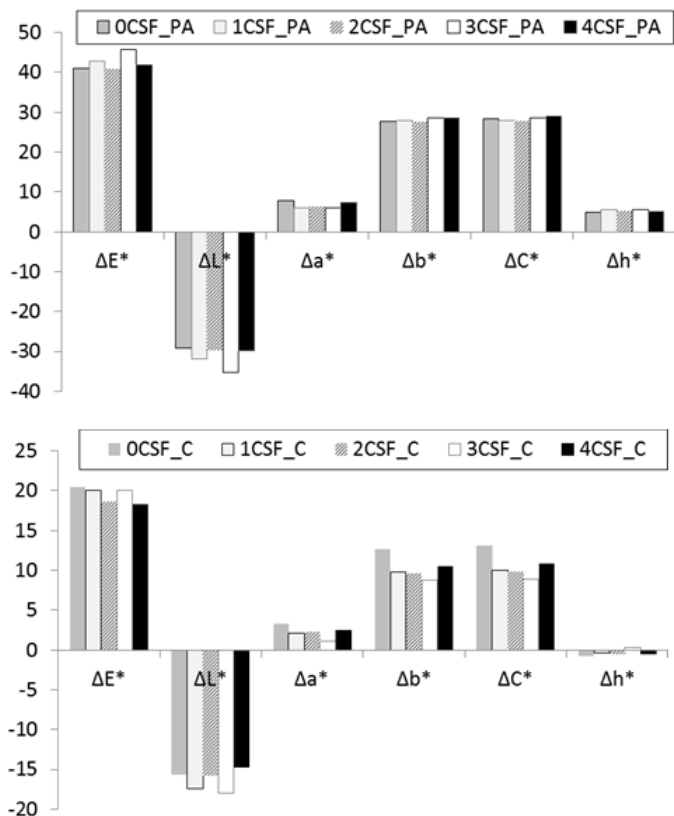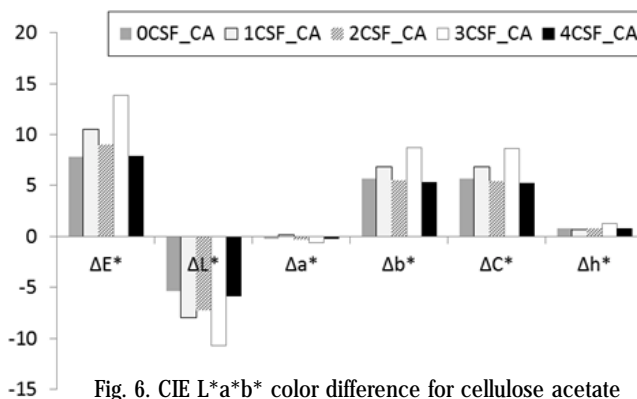

Fig. 5. CIE L*a*b* color difference for cotton samples dyed with brown solution extracted by boiling pomegranate peels, arils with seeds

and mordant respectively, for the calculation of % Strength SUM, one has not used as reference the undyed samples (coded as Reference_W, Reference_PA, Reference_C or Reference_CA), but the dyed samples (coded for each type of material with 0CSF symbols) (table 6).

Table 6 presents the statistical analysis for % Strength SUM corresponding to the samples 1CSF÷3CSF (from each type of studied textile material), dyed with total volume of 120 mL solution (consisting of mordant and CSF brown

solution), using as reference the 0CSF sample dyed only with CSF brown solution (without mordant). The comparisons show the effects exerted by the CSF brown solution and mordant, while when comparing the 4CSF samples with 0CSF afferent to each type of studied textile material, one can only deduce the mordant influence.

By comparing the values of % Strength SUM average for the samples 4CSF and 0CSF respectively (from table 6), one can obtain information about the direction of influence (positive or negative) exerted by mordant. Mordant has a positive influence only in the case of dyeing on wool and

Textile material	Statistical analysis of % Strength SUM average[1]	Sample name[2]				
		0CSF[3] (0:120 as reference)	1CSF (60:60)	2CSF (30:90)	3CSF (90:30)	4CSF (50:120)
Wool	% Strength SUM average	100	109.14	107.17	122.51	108.95
	SD	-	0.0562	5.0863	1.0922	7.2862
	SEM	-	0.0251	2.2746	0.4884	3.2585
	CV	-	0.0515	4.7590	0.9967	7.4766
Polyamide	% Strength SUM average	100	108.09	99.410	99.560	98.896
	SD	-	1.9296	0.4878	3.5122	0.7702
	SEM	-	0.8629	0.2177	1.5707	0.3440
	CV	-	1.7851	0.4897	1.8579	0.7788
Cotton	% Strength SUM average	100	97.500	95.010	93.116	95.010
	SD	-	0.7408	3.7669	1.0009	3.7669
	SEM	-	0.3313	1.6800	0.4476	1.6800
	CV	-	0.7598	3.9647	1.0749	3.9647
Cellulose acetate	% Strength SUM average	100	105.07	110.25	127.13	102.17
	SD	-	6.7432	7.5834	8.7356	1.2516
	SEM	-	3.0165	3.3914	3.9067	0.5597
	CV	-	6.4193	6.8780	5.2268	1.2130

Table 6
STATISTICAL ANALYSIS OF % (COLOR) STRENGTH SUM REVEALED BY THE PARAMETERS SD, SEM AND CV

[1]statistical analysis: standard deviations (SD), standard errors of mean (SEM) and the coefficient of variation (CV);

[2]same codes as in table 1; in parentheses is indicated the volumetric ratio for mordant: CSF brown solution;

[3]0CFS samples (with 0:120 volumetric ratio) were considered as reference samples.

cellulose acetate, a fact also confirmed by the K/S values from tables 2 and 5.

Taking into account that the values of % Strength SUM average depends on K/S_{sample} (according to equation 1), it follows that higher values for the parameters SD, SEM and CV indicate indirectly poorer color uniformities. In this connection, the most uniform dyeing was obtained for polyamide samples.

Conclusions

The decoct (CSF brown solution) obtained by boiling pomegranate peels, arils and seeds can be used to dye wool, polyamide, cotton and cellulose acetate. The FTIR analysis confirms the modifications of the spectra of dyed samples, as compared to those of reference samples for wool and polyamide. The modifications appear at the level of peaks afferent to OH groups, proving the increase of the number of OH groups, because these are attached to natural pigments extracted in decoct. The K/S values of the dyed samples depend on the volumes of decoct used: brown decoct (CSF brown solution as dyeing solution) and nettle decoct (as mordant). The hierarchy of K/S values obtained as the result of dyeing is as follows: wool >polyamide > cotton> cellulose acetate. Mordanting stage performed prior to dyeing stage has a positive influence only in the case of wool and cellulose acetate. Colorimetric measurements (CIE L*a*b* color differences) show that the wool, polyamide and cotton samples are *darker redder yellow*, while the samples of cellulose acetate are *darker less red yellow* than the reference. Both the values of % Strength SUM and the statistical analysis offer indications on the coloring/ dyeing strength of the samples with two types of decoct: of pomegranates and of nettle. The small and very small values of the parameters SD, SEM and CV indicate indirectly better color uniformities.

References

1.TEIXEIRA DA SILVA, J. A., RANA, T. S., NARZARY, D., VERMA, N., MESHRAM, D. T., RANADE, S. A., Scientia Horticulturae, **160**, 2013, p. 85.
2.MENA, P., MARTI, N., GARCIA-VIGUERA, C., Journal of Agricultural and Food Chemistry, **62**, 2014, P. 6936.
3.MARKAKIS, P., Anthocyanins as food colors - Food Science and Technology, Academic Press, New York, 1982.
4.MAZZA, G., BROUILLARD, R., Food Chemistry, **25**, no 3, 1987, p. 207.
5.ZHAO, X., YUAN, Z., FANG, Y., YIN, Y., FENG, L., European Food Research and Technology, **236**, 2013, p. 109.
6.ORDOUDI, S., MANTZOURIDOU, F., DAFTSIOU, E., MALO, C., HATZIDIMITRIOU, E., NENADIS, N., TSIMIDOU, M., Journal of Functional Foods, **8**, 2014, p. 161.
7.LANSKY, E., NEWMAN, R., Journal of Ethnopharmacology, **109**, 2007, p. 177.
8.FISCHER, U., CARLE, R., KAMMERER, R., Food Chemistry, **127**, 2011, p. 807.
9.TURFAN, O., TURKYILMAZ, M., YEMIS, O., OZKAN, M., Food Chemistry, **129**, 2011, p.1644.
10.MITTAL, S., GOYAL, V., SINGH RAJAWAT, D., American International Journal of Research in Formal, Applied & Natural Sciences, **11**, no 1, 2105, p. 55.
11.KAN, C.W., YUEN, C.W.M., Journal of Materials Processing Technology, **178**, 2006, p. 52.
12.HERNANDEZ, F., MELGAREJO, P., TOMAS-BARBERAN, F. A., ARTES, F., European Food Research and Technology, **210**, 1999, p.39.
13.POPESCU, V., PUI, A., SANDU, I.C.A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 2, 2016, p. 270.
14.POPESCU, V., SANDU, I.C.A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 10, 2016, p. 1994.
15.SOMERS, T. C., EVANS, M. E., Vitis, **25**, 1986, p. 31.
16.SKREDE, G., WROLSTAD, R. E., DURST, R. W., Journal of Food Science, **65**, 2000, p. 357.
17.PUSCAS, E.L., Colour Theory and Measurement, Ed. Rotaprint, Iasi, 1983.
18.SCHANDA, J., Colorimetry. Understanding the CIE System, Wiley Interscience, 2007.
19.SANDU, I., SANDU, I.C.A., SANDU, I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.
20.ATODIRESEI, G.V., SANDU, I.G., TULBURE, E.A., VASILACHE, V., BUTNARU, R., Rev. Chim. (Bucharest), **64**, no. 2, 2013, p. 165.
21.SCARLET, R., MANEA, L.R., SANDU, I., CRAMARIUC, B., SANDU, A.V., Rev. Chim. (Bucharest), **63**, no. 8, 2012, p. 777.
22.POPESCU, V., SANDU, I. G., VASLUIANU, E., SANDU, I, CAMPAGNE, C., Rev. Chim. (Bucharest), **65**, no. 12, 2014, p. 1439.
23.POPESCU, V., SANDU, I., Rev. Chim. (Bucharest), **65**, no. 7, 2014, p. 811.
24.POPESCU, V., SANDU, I., MURESAN, E.I., ISTRATE, B., LISA, G., Rev. Chim. (Bucharest), **65**, no. 6, 2014, p. 676.
25.ABDEL-KAREEM, O., International Journal of Conservation Science, **6**, no. 2, 2015, p. 151.
26.*** Color iQC and Color iMatch, Color Calculations Guide, Version 8.0, July 2012, p.14.
27.SAVIUC PAVAL, A.M., SANDU, A.V., POPA, M.I., SANDU, I.C.A., BERTEA, P., SANDU, I., Microscopy Research and Technique, **76**, no. 6, 2013, p. 564.
28.MUNTEANU, M., SANDU, I., VASILACHE, V., SANDU, I.C.A., International Journal of Conservation Science, **7**, SI1, 2016, p. 349.
29.SANDU, I.C.A., BRACCI, S., LOBEFARO, M., SANDU, I., Microscopy Research and Technique, **73**, no. 8, 2010, p. 752.
30.DARQUE CERETTI, E., AUCOUTURIER, M., FELDER, E., BURR, A., ROBCIS, D., THOMAS, C., International Journal of Conservation Science, **6**, SI, 2015, p. 531.
31.POPESCU, G., Programing of PCs in MATLAB; TehnoPress Ed.: Iasi, Romania, 2009.
32.POPESCU, G., Numerical resolvings in MATLAB; TehnoPress Ed.: Iasi, Romania, 2009.
33.HANIFF NISHA, M., TAMILEASWARI, R., JESURANI, Sr.S., International Journal of Engineering Research & Technology, **4**, no. 4, 2015, p. 1044.
34.HWANG, E.K., LEE, Y.H., KIM, H.D., Fibers and Polymers, **9**, no. 3, 2008, p. 334.
35.KULKARNI, S.S., GOKHAL, A.V., BODAKE, U.M., PATHADE, G.R., Universal Journal Environmental Research and Technology, 1, no.2, 2011, p. 135.