Rhus pentaphylla Bark as a New Source of Natural Colorant for Wool and Silk fibers

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Abstract: Natural dye extracted from *Rhus pentaphylla* bark was applied on wool and silk fabrics by an exhaustion dyeing process. Aluminum, tannic acid, and stannous chloride were used as mordants. The dyeing was conducted with and without metallic salt mordants, using three different mordanting methods: pre-mordanting, meta-mordanting, and post-mordanting. A large variety of pale to dark reddish-brown color shades was obtained. The color of each dyed material was scrutinized in terms of the CIELAB (L*, a* and b*) and (K/S) values. The color fastness to washing, rubbing, perspiration, and light of the dyed samples was determined according to ISO standards methods. Optimum results were obtained when dyeing with 7g of the dye at pH 2, a temperature of 100°C during 60 minutes for both wool and silk fibers. Dyeing fastness had mostly been good to very good level with the exception of the fastness to light which was medium.

Keywords: *Rhus pentaphylla*, tannins, natural dyeing, wool, silk, mordanting.

1- Introduction:

Recently, the use of synthetic dyes is more and more decreasing. This is due to the strict environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes [1]. Natural dyes are more eco-friendly than synthetic ones and can show better biodegradability. So, widespread interest has emerged in the dyeing of textile fibers using natural colorants [2].

Natural dyes have a wide range of shades that can be obtained from insects, minerals, fungi and various plant parts including roots, barks, leaves, flowers, skins and fruit-sand shells of plants [3].

Many previous studies have demonstrated the presence of several natural molecules in many plants and vegetable wastes that can be successfully used as a natural colorant for textile fibers such as: betalains and indicaxanthin from mature orange-yellow fruits of *O. ficus-indica* [4], anthocyanin from grape pomace [5], flavonoids from Olive Mill Waste Water [6].

Rus pentaphylla is a tree present with abundance in Tunisia. It spreads in the North and the Center of the country and is relieved by *R. tripartita* from the center to the far southern region. Indeed, the genus *Rhus* is represented by two species: *Rhus tripartita* (Ucria) Grande and *R. pentaphylla* [7]. The two species may be sympatric in several regions and they grow mainly on eroded substrates, under a rainfall ranging from100 to 600 mm/year and at altitudes ranging from 10 to 50 m [8].

Rhus pentaphylla seed, leaf and root aqueous extracts are rich in tannins, flavonoids and coumarins. These natural molecules showed substantial antibutyryl-cholinesterasic activity that could be used for the treatment of Alzeimer’s disease [9].

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In this context, the present paper focuses on the valorization of the flavonoids and tannins present in the aqueous extract of the *Rus pentaphylla* barks in the field of textile dyeing for wool and silk fabrics.

2- Experiment section:

2-1- Materials and chemicals

Prescoured wool fabric (Plain weave and weight, 118 g m^{-2}) and bleached silk fabric (75.2 g m^{-2}, plain weave) were procured commercially.

Rus pentaphylla bark was supplied in December 2013 from Msaken (Tunisia). The collected plant samples were washed, shade dried and grinded to powder form using an electrically operated grinder.

Three different laboratory grade mordants were used: aluminum potassium sulfate ($KAl\ (SO_4)_2{\cdot}12H_2O$), stannous chloride ($SnCl_2{\cdot}5H_2O$) and Tannic acid.

The mordanting and dyeing processes were conducted using a laboratory dyeing machine (Ahiba Data Color International, USA).

The UV–Vis spectra of the aqueous fraction were recorded using a CECIL 2021 Instruments UV/Vis spectrophotometer using quartz cells of path length 1 cm. The CIE L*, a*, b* and color yield (K/S) values of dyed samples were measured using a spectrophotometer with dataMaster 2.3 (Datacolor International, USA) with illuminant D65 at 10 degree observer.

2-2- Plant material

Rus pentaphylla was collected in the region of M'saken (Sousse, Tunisia) in december 2013. The plant was identified by Prof. Fethia HARZALLAH-SKHIRI in the Laboratoire de Biologie Végétale et Botanique, Institut Supérieur Agronomique de Chott meriem, Université de Sousse, Tunisia and a voucher specimen (PL-08) was deposited in the same laboratory.

2-3- Extraction of natural dye from *Rus pentaphylla*

The collected *Rus pentaphylla* bark was used to extract natural colorant. The dye extraction was performed by mixing 5g of the plant material and 100 mL of distilled water and boiling for 1 h. Afterwards, the resulting solutions were filtered to remove the residue and used for dyeing wool and silk fibers.

2-4- Dyeing process

Four experimental dyeing conditions were varied (temperature, dyeing time, pH and dye concentration) to study the dye uptake behavior of *Rus pentaphylla* dye extract on wool and silk fabrics.

2-4-1- Dye amount:

The dye amount was varied from 1g to 10g for 100 mL of distilled water.

2-4-2- pH of the dye bath:

Wool and silk fabrics were dyed in 100 mL of the *Rus pentaphylla* bark aqueous extract at different pH values (2, 3, 4, 5, 6, 7, 8 and 9), at 100°C for 60 min. The pH of the dye baths was adjusted to a desired value with HCl (1M) and sodium hydroxide (0.1 M).

2-4-3- Temperature:

Wool and silk fabrics were dyed at different temperatures (30°C, 40°C, 50°C, 60°C, 70°C, 80◦C, 90◦C and 100°C) using 100 mL of *Rus pentaphylla* bark extract dye solution and at the original pH (equal to 5) of the dye solution for 60 min.

2-4-4- Dyeing time:

To investigate the effect of dyeing time, wool and silk fabrics were dyed for different time intervals (15, 30, 40, 60, 75, 90, 105 and 120 min).

2-5- Mordanting process

Three different mordanting methods were utilised: pre-mordanting, meta-mordanting and post-mordanting, using aluminum potassium sulfate, stannous chloride and tannic acid with a concentration of 3% owf. For the pre-mordanting method, fabrics were impregnated in a mordanting solution at a liquor ratio of 1:40, at 30°C for 45 min before dyeing. In the post-mordanting method, the dyed fabric was subjected to the same treatment. In the case of meta-mordanting, the mordant was added to the dye bath simultaneously with dyeing process.

2-6- Dyeing quality evaluation

Colour values such as L*, a*, b* and (K/S) were measured by SpectroFlash SF300 spectrophotometer. L*, a* and b* represent lightness or luminosity, redness-greenness of colour and yellowness-blueness of colour, respectively.

The colour yield (K/S) value was measured at 410 nm and transferred to (K/S) according to the Kubelka-Munk equation (Kubelka, 1948, 1954):

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

Where R is the decimal fraction of the reflectance of dyed fabric, R_0 is the decimal fraction of the reflectance of non-dyed fabric, K is the absorption coefficient and S is the scattering coefficient.

2-7- Fastness testing

The dyed samples were tested according to standard methods. The specific tests were for colour fastness to washing ISO 105-C06, colour fastness to rubbing ISO 105-X12, colour fastness to light ISO 105-B02 and colour fastness to perspiration ISO 105-E04.

2- Results and discussion:

2-1- Effect of dyeing conditions

2-1-1- Effect of the dye amount

The amount of *Rus pentaphylla* colorant was varied from 1g to 10 g per 100 ml of water. As demonstrated in Fig.1, the color yield (K/S) values increased with increasing dye concentration. The obtained shade of the dyed wool and silk samples were deeper as the initial dye concentration increased up to 7g. After this concentration, the (K/S) values decreased slowly. At 8g or above a plateau value of (K/S) was observed which indicate a saturation state of the fiber in these experimental conditions.

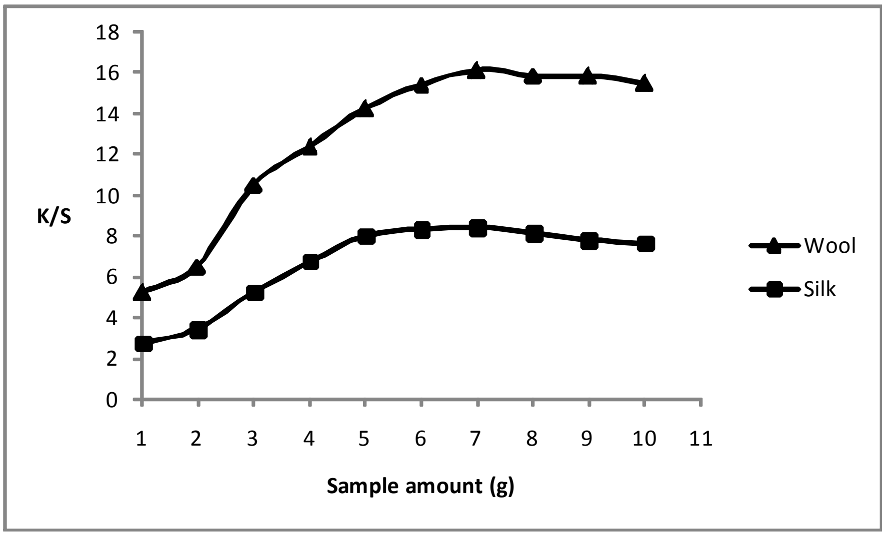


Fig.1. Effect of the sample amount of the dye on the colour yield (K/S)

2-1- 2- Effect of the dye bath pH

The pH of the dye solution is one of the most important parameters controlling the adsorption capacity of dye into proteinic fibers. The effect of dye bath pH on the (K/S) value of the dyed wool and silk fabrics with *Rus pentaphylla* extracts is depicted in Fig. 2. The (K/S) value was highest at pH 2 and decreased with the increasing pH from 3 to 9.

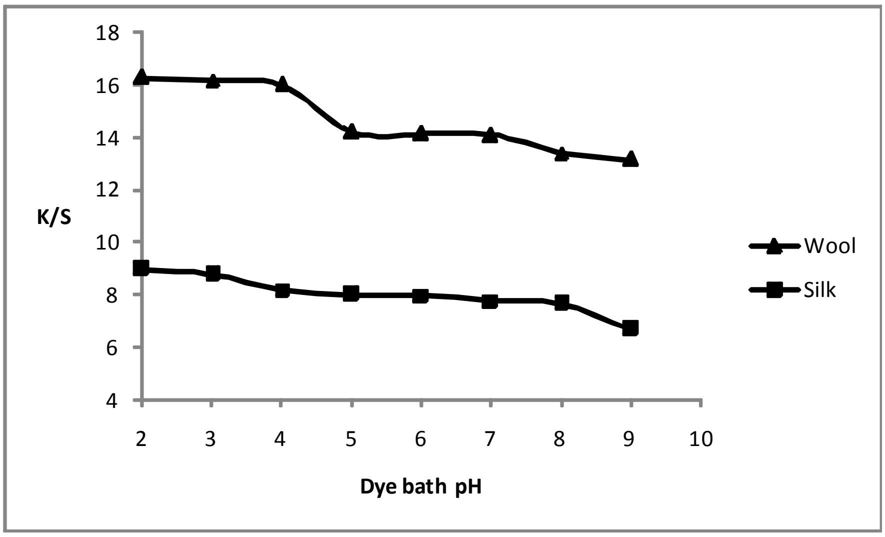


Fig.2. Effect of the dye bath pH on the colour yield (K/S)

This is due mainly to an increase in the protonation of the amino (-NH_2) groups of amino acids in the protein fibers, while the carboxyl groups in the side chains are essentially unionized at lower pH [10]. Whereas in the alkaline solution, reaction with hydroxide ions (OH^-) converts the ammonium ion ($NH3^+$) to amino (NH_2) groups and the fiber contains more carboxylate ions (COO^-) [11]. Thus, electrostatic repulsion between the phenolic colorants and the protein fibers occurs, which leads to a decrease in the dye uptake [12].

Rus pentaphylla extract contains Tannins which are phenolic compounds [9] that can form hydrogen bonds with the carboxyl group of protein fibers. Furthermore, there are two other possibilities involved; (a) the anionic charge on the phenolic groups forms an ionic bond with cationic (amino groups) on the protein substrate; and (b) a covalent bond may also form by an interaction between any quinine or semi-quinone groups present in the tannin and suitable reactive groups on the silk fiber [13].

2-1-3- Effect of the dyeing temperature

Fig. 3 shows the effect of dyeing temperature on the color yield (K/S) values of the wool and silk fabrics dyed with *Rus pentaphylla* extracts. The obtained results showed that increasing temperature increased the color yield (K/S). Based on Fig. 3, the maximum color strength was obtained at 100°C. The color of the dyed silk fabric was reddish-brown.

Indeed, this result may reflect that increasing temperature may increase the by fibre swelling so the mobility of the large dye ions increase with temperature and thus an increase in the number of molecules interacting with the active sites at the surface. So, the diffusion of the dye to the silk increase with higher temperature [10].

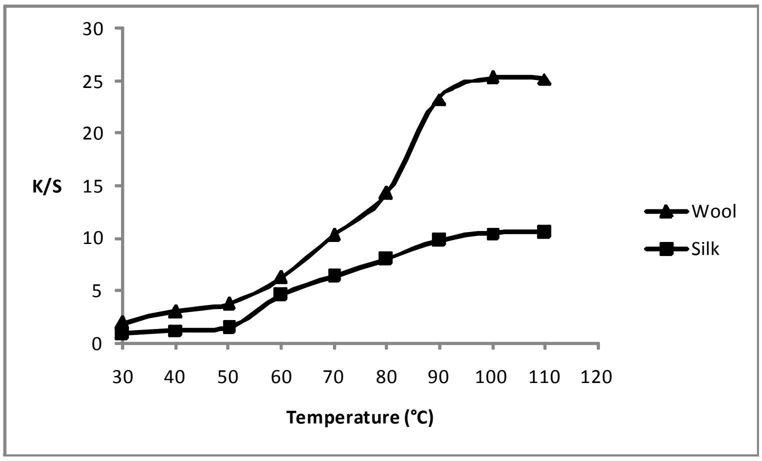


Fig.3. Effect of the dyeing temperature on the colour yield (K/S)

2-1-4- Effect of the dyeing duration

The effect of dyeing duration on the color yield values is shown in Fig. 4. A longer dyeing time means higher color yield (K/S values) until dye exhaustion reaches equilibrium equilibrium, and there is no significant increase after further increases in dyeing time. When fiber was dyed for sufficient time, the dye reaches the fiber structure and it is generally distributed in the interior of the fiber while it remains only on the surface with slight diffusion when dyed for a short time. The optimum time for dyeing of both fabrics was obtained at 60 min.

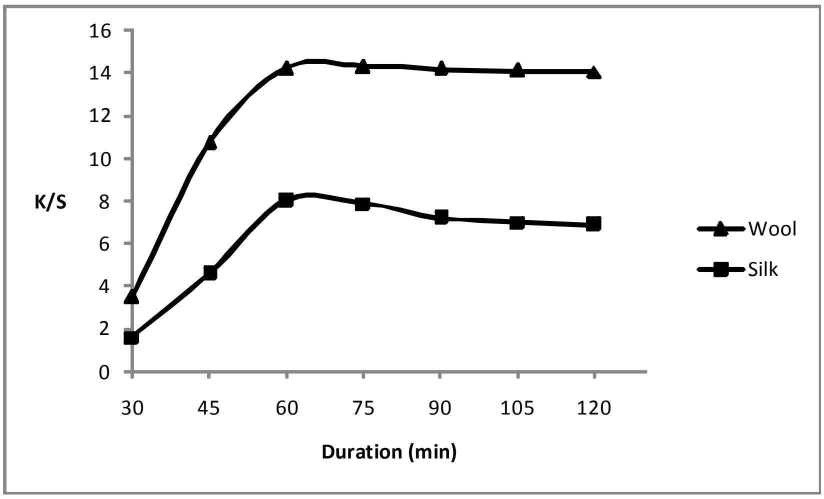


Fig.4. Effect of the dyeing duration on the colour yield (K/S)

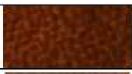
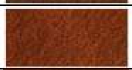
The slight decrease of color yield after 60 min which might be due to desorption of colorant from fabric to the dye bath caused by the long period of the dyeing process, is observed and more pronounced in the case of silk fibers.

2-2- Effect of mordanting treatments

2-2-1- Effect of the mordanting conditions on dyeing properties

Three mordant methods, pre-mordanting, meta-mordanting and post-mordanting were used to dye wool and silk. Alum, tannic acid and stannous chloride are used as mordants. Table 1 and Table 2 show the effect of mordanting methods on dyeing of the two protein fibers with the aqueous extract of *Rus pentaphylla* bark on the colour yield (K/S) and the colorimetric data (*L**, *a**, *b**, *C** and *h**).

Table 1. The dyeing results, obtained shades, the (*K/S*) and the colorimetric data (*L**, *a**, *b**, *C** and *h**) for the dyed wool fibers with and without metallic salts)

Method	Mordant	Samples	(K/S)	L*	a*	b*	C*	h*
Without mordanting			14,20	43.34	23.25	33.16	40.50	54.9
Pre-mordanting	Alum		10,28	44.22	41.22	25.28	26.13	45.9
	Tannic Acid		12,45	43.74	22.50	31.62	38.80	54.57
	Stannous chloride		9,31	45.77	21.19	28.21	35.29	53.09
Meta-mordanting	Alum		12,01	38.48	19.23	20.22	27.90	46.43
	Tannic Acid		12,34	42.97	21.80	29.82	36.94	53.83
	Stannous chloride		8,19	45.77	19.28	24.79	31.40	52.13
Post-mordanting	Alum		16,2	37.23	22.22	27.71	35.52	51.2
	Tannic Acid		14,29	42.67	25.01	32.21	40.78	52.1
	Stannous chloride		14,33	42.80	26.36	32.76	42.05	51.18

It was observed that all the type of used mordants could lead to a variation of red-brownish shades ranging from dark to light. Even for the same mordant and through different types of the mordanting process, shades could change from light to dark.

Table 2. The dyeing results, obtained shades, the (*K/S*) and the colorimetric data (*L**, *a**, *b**, *C** and *h**) for the dyed silk fibers with and without metallic salts)

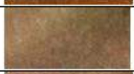
Method	Mordant	Samples	(K/S)	L*	a*	b*	C*	h*
Without mordanting			8,01	55.34	17.45	38.75	42.50	65.7
Pre-mordanting	*Alum*		4,5	57.72	21.53	27.33	34.80	51.77
	Tannic Acid		6,73	56.19	15.54	33.20	36.66	64.9
	Stannous chloride		4,17	59.82	15.39	28.52	32.40	61.64
Meta-mordanting	Alum		5,08	57.39	16.86	22.22	27.90	52.81
	Tannic Acid		6,23	56.86	16.10	32.66	36.42	63.76
	Stannous chloride		3,47	61.42	13.21	23.91	27.32	61.0
Post-mordanting	Alum		6,86	56.13	18.56	32.31	37.26	60.1
	Tannic Acid		6,98	56.02	19.68	35.70	40.76	61.14
	Stannous chloride		7,14	55.55	19.01	31.45	38.23	64.99

Table 1 shows that only in the case of the post-mordanting method, stannous chloride gave a slightly higher color yield value ((*K/S*) = 14,33) than non mordant wool samples ((K/S=14,2). Whereas, as shown Table 2, all the used mordants decreased the obtained color yield (K/S) of silk fabrics for the three used methods of mordanting.

2-2-2- Effect of the mordanting conditions on fastness properties of dyed fabrics

The rating of fastness (washing, rubbing, light, and perspiration fastness) of mordanted and unmordanted wool and silk are shown repectively in Table 3 and Table 4. It was found that the fastness of unmordanted fabrics in both cases (for wool and silk) are considerably good except light fastness which was medium (noted 3 per 8 graduations of the blue scale). Table 3 and table 4show also that mordanting methods improved almost of the fastness properties of the dyed samples with the aqueous extract of *Rus pentaphylla* bark, especially the color fastness to light for silk fibers in the case of post-mordanting with stannous chloride which was doubled.
A probable explanation for the good fastness property is that the aqueous extract of *Rus pentaphylla* bark is rich with phenolic compounds [8] such as tannin and flavonoids which are known to form stable complexes with metal cations. Hence, after mordanting, there is an improving of the fastness properties [14].
In summary, extracts obtained from *Rus pentaphylla* bark were used to dye wool and silk fabrics. The uptake of this natural dye extracts by both of these fibers decreased when the pH increased from 2 to 9. The dyeing temperature of 100 °C and dyeing time of 60 min were appropriate for direct dyeing methods. The dyed wool and silk fabrics had a good color fastness to washing with, rubbing, perspiration and acceptable color fastness to light. All mordanting methods have shown a positive effect on the fastness properties which increased considerably. In nutshell, this aqueous extract of *Rus pentaphylla* bark could be a promising resource to be used as a natural textile dye for proteinic fibers.

Table 3. Fastness properties of the dyed wool samples with and without metallic salts

Method	*Mordant*	*Wash ISO 105-C06*	*Light ISO 105-B02*	*Rubbing ISO 105-X12*		*Perspiration ISO 105-E04*	
				Dry	*Wet*	*Acidic*	*Alkaline*
Without mordanting	-	4	*3*	4	3-4	4	3-4
Pre-mordanting	**Alum**	4-5	4	5	4-5	4	4
	Tannic acid	4-5	4	5	4	4	4
	Stannous chloride	4-5	4	4	4	4	4
Meta-mordanting	**Alum**	4-5	5	5	5	5	4-5
	Tannic acid	4-5	4	5	4-5	4-5	4
	Stannous chloride	4-5	4	4-5	4	5	4
Post-mordanting	**Alum**	4-5	5	4-5	4	4	4
	Tannic acid	4-5	4	4	4	4	4
	Stannous chloride	4-5	5	4	4	5	4

Table 4. Fastness properties of the dyed silk samples with and without metallic salts

Method	*Mordant*	*Wash ISO 105-C06*	*Light ISO 105-B02*	*Rubbing ISO 105-X12*		*Perspiration ISO 105-E04*	
				Dry	*Wet*	*Acidic*	*Alkaline*
Without mordanting	-	4	*3*	4	3-4	3-4	3-4
Pre-mordanting	**Alum**	5	4	5	4-5	4	4
	Tannic acid	4-5	3	5	4	4	4
	Stannous chloride	4-5	3	4	4	4-5	4
Meta-mordanting	**Alum**	4-5	4	5	5	5	4-5
	Tannic acid	4-5	3	5	4-5	4-5	4
	Stannous chloride	4-5	3	4-5	4	5	4
Post-mordanting	**Alum**	4-5	5	4-5	4	4	4-5
	Tannic acid	4-5	5	4	4	4	4
	Stannous chloride	4-5	6	4	4	4	4

4- Conclusion

Extracts obtained from *Rus pentaphylla* bark was used to dye wool and silk fabrics. The uptake of this natural dye extracts by both of these fibers decreased when the pH increase from 2 to 9. The dyeing temperature of 100 °C and dyeing time of 60 min were appropriate for direct dyeing methods. The dyed wool and silk fabrics have good color fastness to washing with, rubbing, perspiration and acceptable color fastness to light. All mordanting methods have shown a positive effect on the fastness properties which increased considerably. Conclusively, this aqueous extract of *Rus pentaphylla* bark could be a promising resource to be used as a natural textile dye for proteinic fibers.

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