Application of *Prunus amygdalus* By-products in Eco-friendly Dyeing of Textile Fabrics

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ABSTRACT: Natural dyes have become an interesting subject of study because of their better ecological properties in comparison to their synthetic counterparts. This article concerns the dyeing of wool, silk, and polyamide fabrics with natural dyes extracted from almond shells and stems. The developed method of dyeing by these extracts is interesting and very attractive for several reasons: firstly, the extracts used are the black liquor discharged from the industries of delignification, which is a chemical process for removing lignin from agricultural wastes to produce a cellulosic fiber; (ii) these natural dyes are renewable and available in large quantities; (iii) this method is economical; and (iv) lastly, the dyeing performances of the obtained dyed textiles are very promising. The color of each dyed material was investigated in terms of the CIELAB coordinates and their fastness properties measured by washing, rubbing, and light.

KEYWORDS: Almond shell, almond stem, fastness properties, natural dyes, residual lignin

1 INTRODUCTION

Lignocellulosic biomass is the most abundant renewable biomass on earth. Yearly, approximately 200 billion tons of residues and wastes worldwide are attributed to forestry and agriculture [1]. Lignocellulosic biomass is composed of cellulose, hemicelluloses, and lignin, as well as other minor components. Among them, cellulose is the most abundant renewable organic material produced in the biosphere and is widely distributed in higher plants, in several marine animals, and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba. Owing to their attractive properties of low density, high strength, high tensile modulus, thermal stability, abundance, eco-friendliness, and sustainability [2, 3], cellulose has many applications such as pharmaceuticals, chemical feed stocks, liquid fuel production [4], papermaking, green composites, and cellulose derivatives [5].

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Pulping is the process of converting lignocellulosic biomass into separated pulp fibers, while chemical pulping achieves fiber separation by dissolving the lignin that cements the fibers together. The chemical pulping process, caustic soda-anthraquinone process, has been used to partially separate the microfibrils from the cell wall, remove natural impurities, and obtain fibers with low lignin and hemicellulose content. It is generally thought that alkali can penetrate the interfibril region and cleave α-ether bonds between lignin and hemicelluloses. Besides alkali treatment, hypochlorite treatment (HClO) for bleaching and disinfection is effective for delignification. Although the soda-anthraquinone process is versatile in dealing with different raw materials coupled with superior pulp quality, it displays certain serious drawbacks such as water pollution.

The discharge of the dark-colored wastewater from these industries into natural streams has caused many significant problems, such as increasing the toxicity, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the effluent, and also reducing light penetration, which has a derogatory effect on photosynthesis. Chlorine and its compounds during

bleaching of pulp react with lignin and its derivatives to form high molecular weight, persistent chlorolignin compounds. The hazardous new compounds formed during this process may cause a deleterious environmental impact that can potentially hamper diverse life forms through the food chain of biota [6]. Thus, it is necessary to remove dyes from wastewater before it is discharged. Several methods, such as coagulation, flocculation, ion exchange, membrane separation, and advanced oxidation, have been reported and attempted for the removal of dyes from effluents [7, 8]. Most of these techniques may be efficient for the removal of dyes, but they are costly and will lead to generation of sludge or formation of by-products. For these reasons, the present study focuses on the valorization of this delignification bath in dyeing application.

With the public awareness of eco-safety and health concerns, eco-friendly natural dyes have to some extent re-emerged as a green alternative to synthetic dyes [9]. At present, the production of natural dyes by direct farming results in substantially high specific cost per kilogram of plant material and per kilogram of dyed material. New strategies are required to establish a technically and commercially competitive process. Use of organic wastes is a promising concept for production of natural dyes with lower specific cost. During this work, two waste materials abundant in Tunisia (i.e., almond shell and almond stem) were studied as a potential source of natural dyes. Almond shell is a lignocellulosic agriculture by-product that does not have industrial application yet, and it is usually incinerated or dumped. It has some interesting features like high volume and low value. According to FAO (FAOSTAT data, 2015), Tunisia is ranked as the 8th largest almond-producing country with about 3.8% of the total world production. In fact, Tunisia's annual production of almond shell has been estimated to about 36.000 tons per year by assuming that the shell has about 60% of the almond fruit weight. Nowadays, almond shell is studied as a low-cost and renewable adsorbent for removing heavy metal [13, 14]. It is also used to remove textile dyes from aqueous solutions [15]. Almond shell and other lignocellulosic materials can be used as a potential source for production of activated carbons [16]. It can also be used as an antioxidant and for antiradical activity [17] and as reinforcement of composite materials [18]. It is reported that the outer green of almond has been used to extract natural dye for dyeing of wool [19, 20]. To the best of our knowledge, no data about the application of almond shell and stem as a natural source for textile dyeing is available in the literature. The findings of this work provide a new area of utilization of large quantities of almond shell and stem that are available as residual material. The contents of the lignin of almond shell and almond stem are 25% and 35%, respectively. The present study focuses on the valorization of this delignification bath in dyeing and fastness properties of polyamide, wool, and silk fibers. In this study, the effects of some experimental conditions (dye bath pH, dye bath temperature and dyeing time) on the dyeability of textile fabrics were investigated. Dyeing with and/or without mordants was examined. The color strength, color coordinates, and fastness properties of the obtained dyed fabrics are evaluated and discussed.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Plant Materials

The almond shell and almond stem used during this work were collected from Monastir (a city located on the central coast of Tunisia) in August 2014 (Figure 1). They were washed and rinsed with distilled water in order to eliminate sand. Then, they were dried under natural conditions during the month of September 2014. After that, the obtained materials were milled and sieved to a granulometry having a size range between 200 µm and 400 µm.

2.1.2 Textile Materials

In this study, bleached samples of wool, silk and polyamide fabrics were procured and used for dyeing. Their physical characteristics are summarized in Table 1.

2.1.3 Chemicals and Reagents

Alum ($KAl(SO_4)_2{\cdot}12H_2O$, Fluka, Germany), Ferrous sulphate ($FeSO_4$, Riedel-de Haën, Germany) and tannic acid ($C_{76}H_{52}O_{46}$, Sigma-Aldrich, Belgium) were laboratory reagents grade and were used without further purification. Commercial Mimosa extract was obtained from Silvateam (Italy). Folin-Ciocalteu reagent, catechin ($C_{15}H_{14}O_6$), vanillin ($C_8H_8O_3$), sodium nitrite ($NaNO_{2)}$, aluminium chloride ($AlCl_3$), acetic acid (CH_3COOH) and methanol (CH_3OH) were purchased from Sigma-Aldrich (Belgium). Gallic acid ($C_7H_6O_5$) and sodium carbonate (Na_2CO_3) were purchased from Fluka (Switzerland). All the chemicals were of analytical grade.

2.2 Methods

2.2.1 Extraction of Natural Dyes

For the two Tunisian agricultural wastes, 5 g of almond shell and/or stem (prepared according to

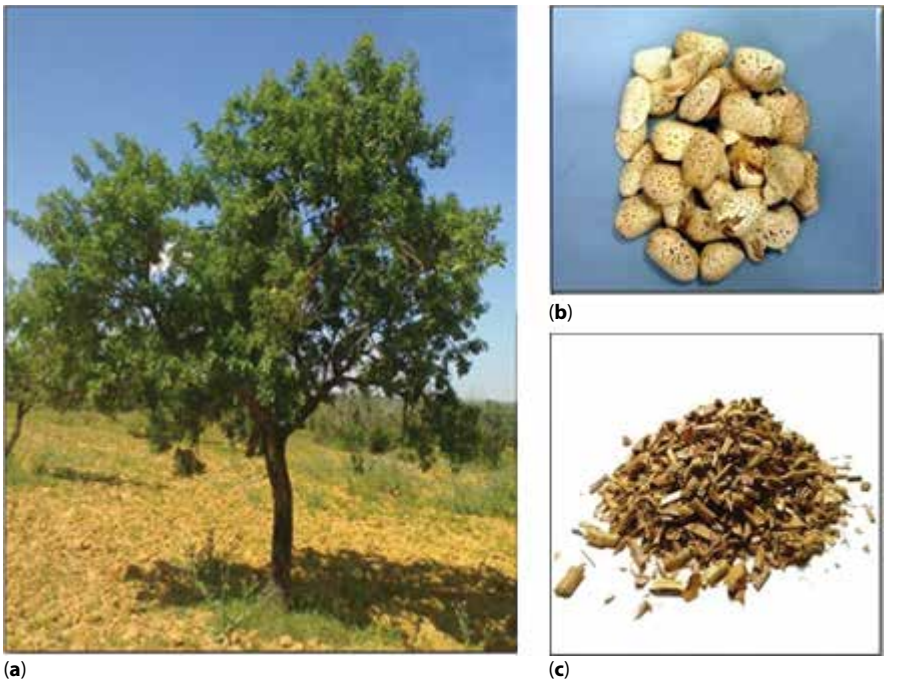

Figure 1 (**a**) *Prunus amygdalus* plant in its natural habitat, (**b**) almond shell, and (**c**) almond stem.

Table 1 Physical characteristics of used fabrics.

Fabrics	Yarn material	Structure	Fabric weight ($g.m^{-2}$)
1	Wool	Plain weave	118
2	Silk	Plain weave	80
3	Polyamide	Single jersey	150

Section 2.1.1) were cooked with 100 mL of alkaline solution (ca. 15% NaOH). The bath temperature was maintained at 100 °C for 60 minutes. After the delignification step, the pulp was separated from the black liquor and the obtained bath was filtrated and recovered. The obtained baths were characterized by the following technical standards and methods.

2.2.2 *UV/Vis Absorption Spectra*

The UV/Vis absorbance spectra of the almond shell and almond stem aqueous fraction were recorded using a CECIL 2021 Instruments UV/Vis spectrophotometer (Cecil Instruments Ltd., United Kingdom).

2.2.3 *Determination of Total Phenolic Content*

The total phenolic content (TPC) in both extracts was determined by Folin-Ciocalteu reagent according to the method of Slinkard and Singleton [21] using gallic acid monohydrate as standard. A 50 µL of extract solution was mixed with 1 ml of distilled water, 0.5 ml of Folin-Ciocalteu reagent, and 2.5 ml of 20% Na_2CO_3. The absorbance of the resulting blue complex was then measured, as described in the method, at 765 nm (using CECIL 2021 Instruments UV/Vis spectrophotometer) after incubation for 20 min at room temperature in the dark. All measurements of the samples were analyzed in triplicate. After a reaction time of 30 min at room temperature, the absorbance was measured again at the same wavelength. Total phenolic content values are expressed as gallic acid equivalents (GAEs), which is a common reference compound.

2.2.4 *Determination of Total Flavonoids Content*

The aluminum chloride colorimetric method was used to determine the total content of flavonoids (TFC). The TFC content was determined using the method described above with slight modification [22]. In fact, a standard solution of catechin (5000 $mg.L^{-1}$) was prepared in methanol, and calibration solutions between 10 and 150 $mg.L^{-1}$ were prepared by dilution with deionized water. Briefly, 0.5 mL of catechin standard solution or sample diluted 1:2 with water was mixed with 2 mL of deionized water and with 0.150 mL of sodium nitrite 5%. After 5 min at room temperature, 0.150 mL of aluminium chloride 10% was added, and after 6 min, 1 mL of sodium hydroxide 1 M was also

added. Deionized water was used to adjust the total volume to 5 mL and absorbance was measured at 510 nm. All measurements were analyzed in triplicate. Total flavonoids content values are expressed as catechin equivalents (CE).

2.2.5 Determination of Condensed Tannins

Condensed tannins were determined according to the Julkunen-Titto method [23]. The test was carried out as follows: 50 µL of each extract was mixed with 1.5 mL of 4% vanillin and then 750 µL of concentrated HCl (ca. 37%) were added. The well-mixed solution was incubated at room temperature in the dark for 20 minutes. The absorbance against blank was determinate at 500 nm. The results were expressed as catechin equivalents (CEs).

2.2.6 The Boehm Titration

The Boehm titration method was applied to determine the surface functional groups containing oxygen. The main principle of this method is that oxygen groups on carbon surfaces have different acidities and can be neutralized by bases of different strengths. Prior to the analysis, samples were dried at 110 °C for 3 h. Then, 0.5 g of each sample was added to glass bottles containing 25 mL of the following 0.05 mol.L^{-1} solutions: NaOH, Na_2CO_3 and $NaHCO_3$. The bottles were sealed and shaken for 48 h to reach equilibrium. Then, the suspensions were filtered and 10 mL of the filtrates were pipetted into 100 mL in Erlenmeyer flasks and the excess acid was back-titrated with 0.05 mol.L^{-1} standard solutions of NaOH. The number of acidic sites was calculated assuming that NaOH neutralizes carboxylic, phenolic, and lactonic groups; $NaHCO_3$ neutralizes carboxylic and lactonic groups; while $NaHCO_3$ neutralizes only carboxylic groups [24].

2.3 Dyeing Method

Three different dyeing conditions were varied (dye bath pH, temperature, and dyeing time) to study the absorption behavior of dyes extracted from almond shell and almond stem by wool, silk and polyamide fabrics. The process of the dyeing step is recapitulated in Figure 2.

2.3.1 Dye Bath pH

In order to have a large study of the pH effect, wool, silk and polyamide fabrics were dyed in 100 mL of aqueous solution at different pH values of 2, 3, 4, 5, 6, 7, and 8, at a liquor ratio of 1:40, at 80 °C for 60 minutes. The pH of the dye baths was adjusted to a desired value by adding acetic acid and sodium carbonate solution. The test was repeated at least in duplicate.

2.3.2 Effect of Temperature

After the effect of dye bath pH, the effect of dyeing temperature was examined. Three different temperatures (i.e., 35, 50 and 90 °C) were chosen using 100 mL of each extract's dye solution at a liquor ratio of 1:40 for 60 minutes. All measurements of the samples were analyzed in triplicate.

2.3.3 Dyeing Time

Several time intervals from 15 to 120 min were taken in order to investigate the effect of dyeing time. All other parameters, such as the pH and temperature, were fixed at the maximum of kinetic dyes.

2.3.4 Dyebath Reuse Procedure

The effect of reusing the dyebath on the color yield (K/S) and the color characteristics of the dyed fabrics was investigated. Five samples were performed at

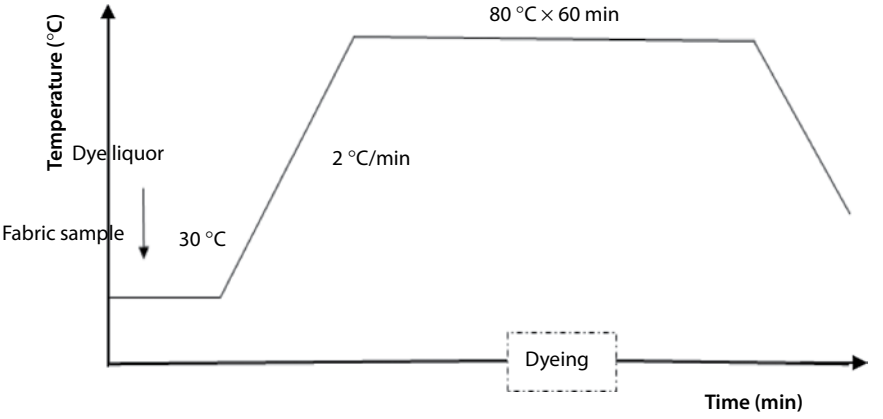

Figure 2 Dyeing process.

optimal conditions of pH = 3, temperature = 90 °C and time = 60 min.

2.3.5 *Mordanting Method*

In the case of mordanting, meta-mordanting was chosen as the most suitable process, especially in the intense natural dyes. Fabric samples were immersed in a bath containing the dye extract and a mordant. The dye bath was maintained at pH value of 3 for 60 min at 90 °C. The fabrics were rinsed, washed with water, squeezed and dried at air room condition (23 °C and 50% humidity). Different mordants including aluminium sulphate hydrate (alum), ferrous sulphate, tannic acid and mimosa were examined and used with a concentration of 3% (w/w with respect to the fabric). All tests were established in triplicate.

2.3.6 *Fastness Properties*

Color fastness of dyed samples was tested according to the ISO standards methods. The specific tests were as follows: ISO 105-C06 for color fastness to washing, ISO 105-X12 for color fastness to rubbing and ISO 105-B02 for color fastness to light.

2.3.7 *Fourier Transform Infrared (FTIR) Spectroscopic Analysis*

The FTIR spectra of the samples were recorded between 4000 and 400 cm^{-1} using a Shimadzu 8400 FTIR Spectrometer, with the processing software Hyper 1.57 (Shimadzu Corporation, Japan).

3 RESULTS AND DISCUSSION

3.1 Characterization of Almond Shell and Almond Stem Aqueous Extracts

Before the evaluation of performance using each aqueous bath obtained after the delignification steps ensuing from the two annual Tunisian agricultural residues, almond stem and shell, the two solutions were characterized in order to (i) identify the chemical groups; (ii) know how these dyes can make a cross-link with the fabric; and (iii) how to justify the solidity efficiency.

3.1.1 *Total Phenolic, Flavonoid and Condensed Tannin Contents and Boehm Titration*

Total phenolic content, total flavonoid content and condensed tannin content were determined from the calibration curves of gallic acid ($Y = 0.0044x + 0.031$; $R^2 = 0.99$), quercetin ($Y = 0.0288x + 0.0058$; $R^2 = 0.99$) and catechin ($Y = 0.00706x + 0.01044$; $R^2 = 0.99$), respectively. The total phenolic, total flavonoid and condensed tannin contents among the different extracts are presented in Table 2. The results showed that almond stem extract possessed the highest phenolic, flavonoid and condensed tannin components. The dark-brown colored almond stems extract is chemically related to flavonoid and tannin compounds, while the Peruvian colored almond shell extract is chemically related to the very limited condensed tannin compounds compared to the total flavonoid content. The analysis of each extracted bath dye was investigated by the determination of acidic groups using the Boehm titration. The result was summarized in Table 3. From this table, different conclusions were stated: (i) the number of acidic sites was the sum of the acidic functional groups: carboxylic, lactonic and phenolic groups; (ii) two extracts have an acid character; moreover, (iii) the almond stem extract presented the highest number of acidic sites, which confirms that this natural dye possessed a higher affinity for protein fibers than the almond shell extract.

Table 2 Total phenolic, flavonoid and condensed tannin contents of almond shell and almond stem extracts.

	Almond shell	Almond stem
Total phenolic content (mg GAE/mg extract bath dye)	0.323	0.632
Total flavonoid content (mg CE/mg extract bath dye)	0.080	0.450
Condensed tannin content (mg CE/mg extract bath dye)	0.008	0.023

Table 3 Boehm titration of extracts.

	Almond shell	Almond stem
Carboxylic ($\times 10^{23}$/g)	0.253	1.217
Lactonic ($\times 10^{23}$/g)	0.181	1.019
Phenolic ($\times 10^{23}$/g)	0.193	0.381
Number of acidic sites ($\times 10^{23}$/g)	0.627	2.617
Number of basic sites ($\times 10^{23}$/g)	0.175	0.675

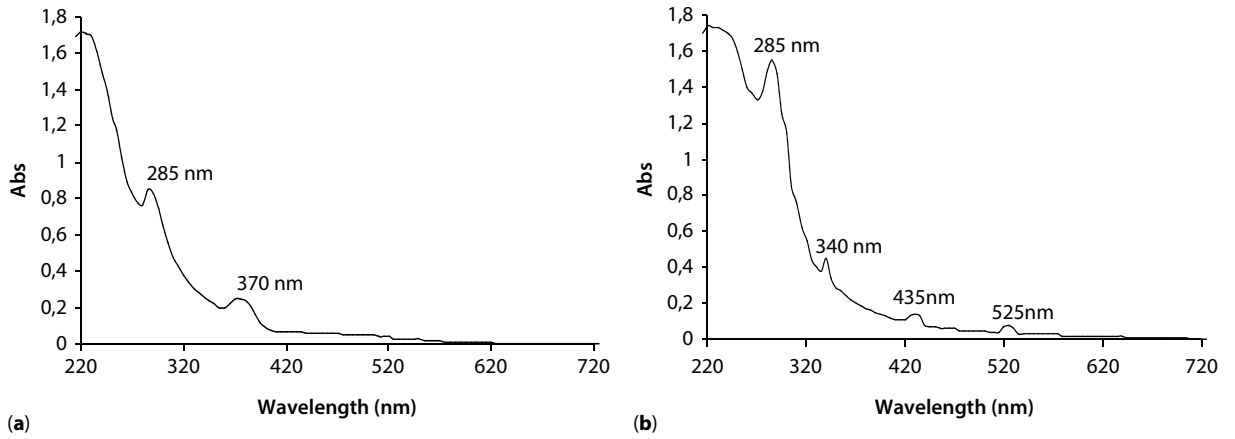

Figure 3 UV-visible spectra of (**a**) almond shell and (**b**) almond stem aqueous extracts.

3.1.2 UV-Visible (UV-Vis) Spectra and FTIR Spectroscopic Analysis

The two aqueous fractions were characterized by UV/Vis spectroscopy. The UV/Vis spectra used were recorded from 220 nm to 720 nm and the results are presented in Figure 3.

Results showed that the almond stem and almond shell aqueous extracts are characterized by color ranging from light to dark browns. These colors are chemically related mainly to polymers of phenolic compounds and tannins polymerization [25, 26]. Generally, phenolic compounds include many great organic substances that have the common characteristic of possessing an aromatic ring with one or more substituent hydroxyl groups and a functional side chain. The UV-Vis spectrum of almond shell extract shows absorptions in the 270–290 nm and 350–370 nm regions. Absorption in the 270–290 nm region may be attributed to the electronic transitions of benzene and its derivatives, which may include various aromatic compounds such as phenolics [27]. Absorption in the 350–370 nm regions may be attributed to the presence of flavonoids related in the extract solution. In the case of almond stem, the UV-Vis spectrum of the aqueous extract also showed two major peaks in the visible region at 435 and 525 nm. The FTIR spectra were used in order to identify the functional group presence in the aqueous media. The FTIR spectra of almond shell and almond stem extracts are represented in Figure 4.

The FTIR spectra of all samples showed that the footprints are most related to the characteristic of lignin. The peak within 1710 cm^{-1} corresponded to -COOH stretching of the ferulic and p-coumaric acids in lignin. The band at 1460 cm^{-1} has arisen from methyl group deformations and lignin aromatic ring vibrations. In addition, the peaks at 1603 cm^{-1} attributed to C=O stretching, 1519 cm^{-1} related to aromatic skeleton vibrations, and 1250 cm^{-1} originating from C-O stretching in guaiacyl ring further indicated the presence of lignin and hemicellulose. The stronger intensity of these signals clearly showed the higher amount of non-cellulosic component [28, 29]. Other characteristic bands related to the chemical structure more than lignin were also detected, especially when it is believed that the lignin can easily associate with other polysaccharide compounds such as hemicellulose stretching at 1510 cm^{-1}, the coniferyl aromatic nucleus wagging at 1235–1275 cm^{-1}, the C-C, C=O, C-H wagging at 1061–1191 cm^{-1}, and the hydrogen-bonded OH stretching at 3750–3332 cm^{-1}.

3.2 Effect of Dyeing Process Conditions on the Obtained Color

3.2.1 Effect of Dye Bath pH

In this section, a series of dyeings were carried out on wool, silk and polyamide fabrics using natural dyes extracted from almond shell and almond stem. In each case, different values of dye bath pH were tested. The effect of the dye bath pH on the color yield (K/S) and the CIE $L^*a^*b^*$ coordinates of the dyed fabrics are reported in Table 4. Obtained results revealed that the K/S value decreased with the increase of the dyeing bath pH. The highest value of K/S was obtained at pH 2. In addition, the luminosity L^* increased. For the parameters a^* and b^*, it appears that these two coordinates decreased with the increasing of the dye bath pH. This effect of dye bath pH can be attributed to the correlation between dye structure and protein fibers (wool and silk). The polyphenolic compounds, which are soluble in water containing hydroxyl groups, were the main dye species present in each bath dye. Moreover, their molecular structures presented an important electronic density and due to their highly

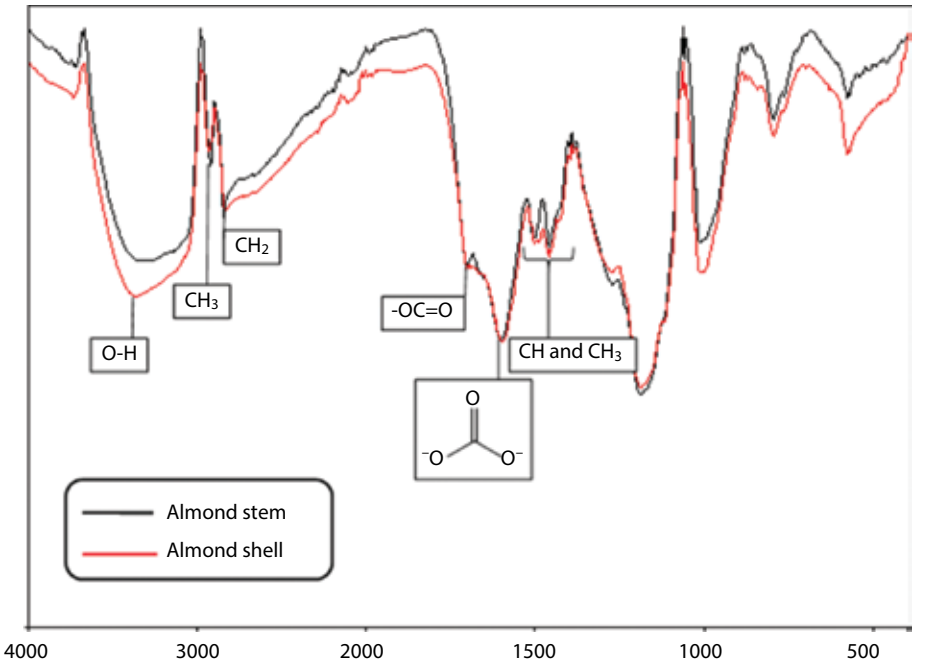

Figure 4 FTIR spectra of almond shell and almond stem extracts.

Table 4 Effect of the dye bath pH on the color yield (K/S) and the CIE L*a*b* parameters.

		Wool				*Silk*				*Polyamide*			
	Dye bath pH	*K/S*	*L**	*a**	*b**	*K/S*	*L**	*a**	*b**	*K/S*	*L**	*a**	*b**
Almond shell	2	5.99	50.98	15.33	23.56	4.82	53.49	13.71	25.28	4.18	51.97	12.12	20.63
	3	5.19	52.37	14.64	20.42	4.99	54.20	13.05	23.12	3.99	52.79	11.43	19.69
	4	5.27	53.92	13.70	17.37	4.62	54.29	12.81	22.07	3.85	53.48	10.38	17.85
	5	3.84	55.51	12.90	15.56	3.35	57.51	12.29	20.36	3.40	54.25	10.13	16.95
	6	4.94	56.17	12.05	14.50	2.81	61.88	12.00	19.88	3.93	55.15	9.81	14.56
	7	1.99	67.27	11.16	8.52	1.46	71.20	9.38	17.95	3.19	57.58	9.17	13.63
	8	1.16	78.62	8.26	6.65	1.27	75.92	7.41	16.00	2.32	64.02	9.11	12.83
Almond stem	2	25.38	34.81	21.26	29.38	19.66	36.58	20.40	28.69	13.79	35.49	16.78	20.64
	3	24.33	35.49	20.62	28.22	18.66	37.58	20.40	28.69	12.36	36.59	16.53	19.73
	4	22.96	36.30	19.89	27.96	18.57	37.67	19.59	27.95	12.35	37.43	15.72	19.49
	5	16.20	38.92	19.69	27.54	17.50	38.96	19.43	26.25	11.26	37.78	15.26	18.76
	6	18.59	39.82	19.62	26.06	16.24	39.29	19.33	25.68	10.83	40.42	14.75	18.28
	7	18.86	40.51	19.19	25.57	12.67	43.96	18.57	27.50	10.39	41.43	14.60	17.00
	8	5.36	47.76	17.57	11.26	3.79	55.43	17.90	17.78	6.27	43.01	14.09	11.03

conjugated system, protein fibers have an amphoteric character. It can be noticed that at pH inferior to isoelectric pH (wool, i.e., pH = 4.6 and silk, i.e., pH = 4.1), protein fibers (wool and silk) contain protonated terminal amino groups. It was found that at pH 3, the polyphenolic compounds possessed a high affinity for protein fibers, which is clearly observed in Table 4 and which justified the obtained maximum color yield. This can be attributed to the important attraction of both the protonated terminal amino groups of fibers and the hydroxyl groups of dyes and a strong crosslink which can be occurring. However, when the pH of the dyeing bath increases more than isoelectric pH, dyeability decreased because of the decreasing number of protonated terminal amino groups of fibers (wool and silk), and therefore the

attraction decreased. That is why in the alkaline solution the number of protonated terminal amino groups of protein fibers (wool and silk) was limited and fibers contained more carboxylate groups (COO^-) [31]. Therefore, an electrostatic repulsion between the anionic dyes and the protein fibers (wool and silk) can take place, which leads to a decrease in the dye uptake. Based on these results, the pH of the dye bath in all experiments was kept at 3 in order to reserve a good dyeing condition and, at the same time, preserve the mechanical properties of used fabric. This same pH was also determined in the case of polyamide fibers dyed with the same natural dyes. The color yield (K/S) of the dyed polyamide fabrics seemed to be inversely proportional to the pH of the dye bath. It could be observed that when the pH of the dyeing bath increased, the dyeability decreased. The effect of the dye bath pH could be attributed to the interaction between polyamide fabric and polyphenol structures present in these aqueous extract solutions. Indeed, polyamide fibers contain protonated terminal amino groups, which make it possible to dye these fibers with the same dyes of wool, which are almost operated at acidic pH.

3.2.2 *Effect of Dyeing Temperature*

In the same manner as in the previous section, dyeing temperature was varied to test its effect on the dyeing properties of the colorants extracted from almond shell and almond stem. Obtained results are recapitulated in Table 5. They clearly indicate that the color strength value (K/S) increased with the increasing of the dye bath temperature. The maximum color strength value was obtained at 90 °C. Generally, this increase of dyeability can be explained by the good diffusion of dyes in side fiber which was submitted by morphological swelling and consequently a good dye diffusion [11], especially in the case of natural fibers (wool and silk). Moreover, in the case of polyamide, the temperature presents important parameters. When the temperature exceeds the glass transition, a good facility of penetration of dyes may have taken place. The best temperature result was noticed at 90 °C. From Table 5 it can also be observed that when the dyeing temperature increases, the luminosity L^* and the parameter b^* decrease, though there is no clear effect on a^* values.

3.2.3 *Effect of Dyeing Duration*

Dyeing time has an effect on the color yield (K/S) and the colorimetric parameters L*, a* and b* of the dyed wool, silk and polyamide fabrics. From Table 6 it can be concluded that the color yield increased as the dyeing time increased. It should also be noted that the dye exhaustion attained a maximum at 60 min and there is no significant increase after further increases in dyeing time over this value. This same effect was excepted as reported in many studies [32, 33]. The colorimetric parameters a^* and b^* exhibited the same behavior as the color yield (K/S). Concerning the luminosity L^*, their values decreased when the dyeing time was raised. In addition, it was found that the K/S values of wool, silk and polyamide fabrics dyed with almond stem extract are higher than the K/S values of wool, silk and polyamide fabrics dyed with almond shell extract, respectively. This result might be attributed to the quantity of phenolic compounds in the almond stem extract, which is more important than that of the almond shell extract, which is also confirmed by FTIR analysis, which at band 1710 cm^{-1} is associated with carboxylate groups.

3.3 Effect of Dye Bath Reuse Number

As the almond stem extract is an effluent which contains a large amount of natural colored substances, verifying the possibility of reusing the dye bath again is indispensable. Indeed, it is very important to exploit the maximum amount of natural colored substances on wool, silk and polyamide dyeing before rejecting/discharging the residual bath. Table 7 shows the effect

Table 5 Effect of the dye bath temperature on the color yield (K/S) and the CIE L*a*b* parameters.

	Dye bath temperature (°C)	*Wool*				*Silk*				*Polyamide*			
		K/S	*L**	*a**	*b**	*K/S*	*L**	*a**	*b**	*K/S*	*L**	*a**	*b**
Almond shell	*35*	1.61	78.46	8.05	4.64	1.86	72.43	8.82	25.26	1.45	73.11	7.71	21.69
	50	2.69	69.51	10.30	13.02	3.42	64.58	12.23	28.28	2.76	65.07	10.24	25.50
	90	8.25	49.72	13.93	22.63	6.31	66.00	14.54	29.01	6.07	48.67	12.68	27.56
Almond stem	*35*	5.48	58.70	10.52	22.16	6.48	61.70	13.52	29.16	5.48	62.70	12.52	27.16
	50	10.68	55.98	12.29	24.04	10.09	50.35	19.69	32.07	7.04	52.87	16.89	29.29
	90	27.84	27.93	18.32	37.83	21.11	36.38	22.54	38.08	15.51	36.12	19.66	33.83

Table 6 Effect of the dyeing time on the color yield (K/S) and the CIE L*a*b* parameters.

	Dyeing time (min)	Wool				Silk				Polyamide			
		K/S	L*	a*	b*	K/S	L*	a*	b*	K/S	L*	a*	b*
Almond shell	15	2.72	71.96	9.13	10.75	1.95	70.75	9.80	19.79	2.00	65.37	8.73	19.03
	30	3.31	69.51	10.15	12.12	3.02	69.81	9.79	19.02	3.48	61.99	9.61	19.32
	45	5.17	69.11	11.69	16.76	4.37	68.93	9.87	20.28	4.17	58.68	10.41	20.25
	60	8.25	49.72	13.93	22.63	6.31	66.00	14.54	29.01	6.47	48.67	12.68	27.56
	90	8.40	47.57	14.50	24.57	6.66	58.82	10.77	30.31	6.63	48.11	13.83	29.10
	120	8.83	43.30	15.19	25.36	6.91	56.92	10.77	31.77	6.93	47.75	14.10	29.46
Almond stem	15	10.88	58.65	9.14	23.99	8.82	51.93	13.95	25.76	8.82	51.93	13.95	25.76
	30	15.38	55.83	11.85	26.36	13.87	51.18	15.36	26.60	9.97	49.74	13.88	24.41
	45	21.06	56.07	10.86	27.22	16.85	56.34	10.94	28.38	12.89	48.29	13.96	24.21
	60	27.84	27.93	18.32	37.83	21.11	36.38	22.54	38.08	15.51	36.12	19.66	33.83
	90	27.98	25.06	19.47	40.94	21.80	35.97	25.72	39.15	15.82	35.26	21.45	34.03
	120	28.08	23.45	21.97	43.70	21.74	33.56	25.80	42.55	15.97	33.32	22.62	35.43

Table 7 Effect of reuse number of the dye bath on the color yield (K/S) and the CIE L*a*b* parameters of fabrics dyed with almond stem extract.

Reuse number	Wool				Silk				Polyamide			
	K/S	L*	a*	b*	K/S	L*	a*	b*	K/S	L*	a*	b*
1	27.98	25.06	19.47	40.94	21.80	35.97	25.72	39.15	15.82	35.26	21.45	34.03
2	25.38	28.83	18.85	40.36	19.87	37.03	24.36	38.60	13.97	38.74	20.88	34.41
3	24.06	29.07	16.86	39.22	18.85	37.72	23.94	38.38	12.89	39.29	19.96	34.21
4	21.84	31.93	15.32	39.83	15.11	38.09	21.54	38.08	11.51	40.12	18.66	33.83
5	19.96	33.06	14.47	38.94	13.82	40.26	20.72	37.15	10.81	42.26	17.45	33.03

of reuse number on the color yield and color characteristics of the dyed fabrics with the almond stem extract. It seems clear according to this table that the color yield (K/S) decreases slightly every time the residual dye baths were reused in a new dyeing process. This can be attributed to the decrease of colored substances in the residual dye bath. Consequently, multiple reuses of the residual dye baths allow obtainment of different nuances of colored samples with decreasing values of a* and b* and increasing values of L*. This result proved that the almond stem extract could be exploited many times to dye textile fibers.

3.4 Study of the Effect of Mordanting

3.4.1 *Effect of Mordanting on Dyeing Properties*

In this study, simultaneous metal mordanting was used to dye wool, silk and polyamide fabrics with almond shell and almond stem extracts. Alum, ferrous sulphate, tannic acid and mimosa extract are used as mordants. Table 8 shows the effect of mordanting treatment on samples (wool, silk and polyamide fabrics) dyed with the aqueous extract of almond shell and almond stem in terms of their color yield and their colorimetric coordinates. It can be noticed that in the case of wool warp versus weft yarns the dye is picked up differently. Thus, a difference is made in the effect of porosity in fabric. In addition, it was observed that the large difference of shades of the dyed fabrics (from the almond stem versus the almond shell) can be attributed to the difference of quality bath obtained from each residue. And, a large distinction can also be observed for all the types of mordants used, which could lead to a variation of brown shades ranging from dark to light. Using ferrous sulphate and tannic acid can increase the color yield of dyed fabrics. On the contrary, using alum and mimosa extract as mordants decreases the color yield. In all cases, the use of ferrous sulphate gave the highest yield of shade value. The K/S values of the wool,

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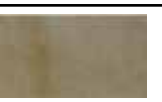
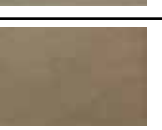
Table 8 Shades, color yield values, and colorimetric coordinates obtained for the wool, silk and polyamide fabrics dyed with and without mordants.

		Almond stem					*Almond shell*				
	Mordant	*Shade*	*K/S*	*L**	*a**	*b**	*Shade*	*K/S*	*L**	*a**	*b**
Wool	*Without mordant*		25.38	34.81	21.26	29.38		5.99	50.98	15.33	23.56
	Alum		22.85	34.81	21.26	29.38		4.58	52.81	16.54	21.28
	Ferrous sulphate		27.84	34.81	21.26	29.38		7.48	48.17	13.61	25.88
	Tannic acid		26.24	34.81	21.26	29.38		6.42	49.81	14.61	24.48
	Mimosa		24.75	34.81	21.26	29.38		4.57	55.12	17.64	20.47
Silk	*Without mordant*		19.66	36.58	20.40	28.69		4.82	53.49	13.71	25.28
	Alum		18.24	37.25	18.23	30.81		3.94	54.22	14.27	25.78
	Ferrous sulphate		21.54	34.87	22.51	23.51		6.42	50.28	15.28	23.75
	Tannic acid		20.24	35.12	21.54	25.21		5.14	52.21	14.24	24.58
	Mimosa		19.66	36.58	20.40	28.69		4.82	53.49	13.71	25.28
Polyamide	*Without mordant*		12.92	36.92	16.82	20.06		5.48	52.78	12.21	20.39
	Alum		12.01	37.8	15.02	22.08		4.25	53.24	13.82	24.48
	Ferrous sulphate		13,86	35.81	13.52	23.29		5.14	50.28	15.28	23.09
	Tannic acid		14.84	34.27	12.68	23.63		5.84	51.74	13.48	24.87
	Mimosa		11,14	38.94	13.38	20.17		5.71	52.02	13.27	24.76

silk and polyamide fabrics increased in the following order:

Ferrous sulphate > Tanic acid > Mimosa> Alum

These results confirm that the ferrous sulphate is the best mordant. Indeed, this mordant is well known for its ability to form coordination complexes and to readily chelate with the dye. As the coordination numbers of ferrous sulphate is 6, some coordination sites remain unoccupied when they interact with the fiber [34]. Functional groups such as amino and carboxylic acid on the fiber can occupy these sites. Thus, the metal can form a ternary complex on which one site binds with the fiber and the other site binds with the dye [35]**.** With ferrous sulphate, the color shade was darker and duller. This may be associated with the change of ferrous sulphate into a ferric form by reacting with oxygen in the air. Ferrous and ferric forms coexist on the fiber and their spectra overlap, which results in a shift of λ_{max} and thus consequently a color change to a darker shade [36]. Additionally, the tannins in the extracts combine with ferrous salts to form complexes, which also result in a darker shade of fabric [37]. The decrease of K/S with using alum and mimosa as mordants may be due to the ability of mordant to form coordination complexes between both the hydroxyl groups of the dye molecules and the fibers functional groups such as amino and carboxylic acid groups. Such a strong coordination tendency can enhance the interaction between the fiber and the dye, resulting in high dye uptake [38].

3.4.2 Effect of Mordanting on Color Fastness

The results of light fastness, washing fastness and rubbing fastness properties of samples dyed with almond shell and almond stem extracts with and without mordants are given in Table 9. These results were evaluated according to ISO standards methods with the grey scale values (rating 1–5: 1 = poor, 5 = excellent) for washing fastness and rubbing fastness, and the blue scale values for light fastness (rating 1–8: 1 = poor, 8 = excellent). Obtained values revealed that washing and dry rubbing fastness properties of fabrics dyed with almond shell and almond stem were in the range of 4 to 5 (good to very good). This good fastness to washing and dry rubbing can be attributed to the fact that these dyes contain phenolic compounds that can form hydrogen bonds with the carboxyl group of protein fibers. Furthermore, there are two other possibilities involved: (i) the anionic charge on the phenolic groups forms an ionic bond with cationics (amino groups) on the protein substrate; and (ii) a covalent bond may also be taking place by an interaction between any quinone or semi-quinone groups present in the tannin and suitable reactive groups on the fiber [39]. However, the light fastness was only fair (3 to 4), as shown in Table 9. Generally, it is well known that the medium light fastness was a major inconvenience of natural dyes. When comparing the fastness values of the samples dyed with and without mordants, it can be observed that the mordanting step slightly improved wash, light and rubbing fastness.

4 CONCLUSION

The target of this work was the search for greener alternatives to satisfy consumer demand for eco-friendly and sustainable products. Progress has been made with this study in the use of *Prunus amygdalus* by-products (shell and stem) extracts for dyeing

Table 9 Color fastness properties of the dyed samples with and without mordants.

		Wash fastness ISO 105-C06	*Light fastness ISO 105-B02*	*Rubbing fastness ISO 105-X12*	
	Mordant			*Dry*	*Wet*
Almond shell	*Without*	4–5	3	4	3
	Alum	4	3	4	3
	Ferrous sulphate	5	4	5	4
	Tannic acid	4-5	4	4-5	3-4
	Mimosa	4	3	4	3
Almond stem	*Without*	4–5	3-4	4-5	3-4
	Alum	4–5	3-4	4	3
	Ferrous sulphate	5	4-5	5	4
	Tannic acid	4–5	4	4-5	3-4
	Mimosa	4	3	4	3

with the advantage of economizing the cost of delignification waste treatment. The color yield of dyed samples was generally high and the obtained shades were brown. The study of the effects of different factors on dyeability of wool, silk and polyamide by the lignin of almond shell and almond stem showed that the pH and the temperature of dye bath as well as the dyeing time considerably affected the color yield. The best results were obtained at pH 3, 90 °C and 60 minutes. Besides, it was found that the developed dyeing process offers better environmental impact as it helps in the uptake of much dye and efficiently reuses dye bath. The wash and dry rubbing fastness of the dyed fabrics ranged from good to excellent, while light and wet rubbing fastness was fair to good. The use of mordants in conjunction with extracts enhances the dyeability and the fastness properties.

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