Middle-East Journal of Scientific Research 21 (9): 1600-1604, 2014
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2014.21.09.21735

Dyeing Properties of Cationized and non Cationized Cotton Fabrics Dyed with *Vitis vinifera* L. Leaves Extract

Mansour Rym, Mhenni. Farouk and Ezzili M. Bechir

[1]Unité de recherche 12-04, Chimie Appliquée et Environnement,
Faculté de sciences de Monastir, Monastir 5000, Tunisie,
[2]CBBC TechnoparcBorjCidria, BP 901-2050, HammamLif Tunisia

Abstract: The present paper lays bare two main objectives. The first is to determine the amount of anthocyanins in the leaves of *Vitis vinifera* L. by the spectrophotometric method and the second is to dye cationized and non-cationized cotton fabrics with the *Vitis vinifera* L. leaves aqueous extract. We have thoroughly investigated the effects of dye bath pH and temperature on the dyeing proprieties of the aforementioned fabrics. The color strength (K/S value) of dyed cationized cotton fabrics (k/s= 12) has been better than the non cationized ones (k/s= 4). Experimental results show that the fastness properties of dyed cationized cotton fabrics range from average to good. We find that the cationization of cotton fabrics has largely improved the dyeability and fastness properties of cotton fabrics dyed with *Vitis vinifera* L. leaves aqueous extract. *Vinifera* L. leaves.

Key words: *Vitis vinifera* L. leaves · Anthocyanins · Cationized cotton · Dyeing · Fastness

INTRODUCTION

The use of plants, seashells and coccid insects to create color is common to all civilizations [1]. With the advent of widely available and cheaper synthetic dyes in 1856; the use of natural dyes with poor to moderate wash and light fastness declined drastically and was replaced by more moderate to excellent color fastness properties of synthetic materials, Yet, it is primordial to note that the revival of natural dyes was mainly due to the hazardous and cancerogenic nature of synthetic dyes.

Vitis vinifera L. is a naural dye-- *by excellence*. It is a woody winter-deciduous climber with tendrils attaching to surrounding plants. It is generally believed to be native to south-western Asia. The leaves are alternating, palmately lobed, 5–20 cm long and broad. The leaves of *vitis vinifera* L. are rich in tannins, flavonoids, procyanidins and also contain organic acids, lipids, enzymes and vitamins [2, 3]. Vine leaves turn red in autumn and their flushing intensities depend on the period of collection [4]. The main coloring agents in *Vitis vinifera* L. leaves are anthocyanins: monoglucoside cyanidin, monoglucoside peonidin and monoglucoside malvidin [5, 14]. Moreover, anthocyanins production in *Vitis vinifera* L. leaves increases in response to surging sugar concentrations in autumn. In this work, *Vitis vinifera* L. leaves were collected, extracted with water and studied to explore their potential applications as natural dyes in textile industry.

Generally, leaves containing primarily anthocyanins appear red, while those with large amounts of both anthocyanins and carotenoids have orange color. However, leaves with carotenoids and little or no anthocyanins are yellow. Anthocyanins contain anthocyanidins (or aglycons) which are basic functional chemical structures in anthocyanins [2]. When anthocyanidins are bonded to a sugar moiety they are known as cyanidins. Cyanidins are important coloring components of *Vitis vinifera* L. leaves (Figure 1). Cotton can be easily dyed, but the cellulose-dye bond is not very strong. Natural cellulose fibers are negatively charged because of the presence of carboxyl and hydroxyl groups [6]. Using commercial cationic agents in the pretreatment of cotton may enhance dye absorption and

Corresponding Author: Unité de recherche 12-04, Chimie Appliquée et Environnement,
Faculté de sciences de Monastir, Monastir 5000, Tunisie.

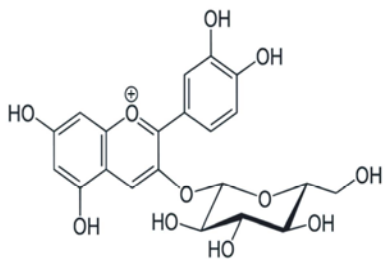

Fig. 1: Chemical structure of one of the Colour compositions of *Vitis vinifera* L. leaves extract dye: Cyanidin-3-oglycoside

can not only increase the dyeing color strength but also improve wash fastness [7]. Cationic modification is a method that has been employed in order to change the surface charge of cellulosic ?bers [8-11]. In these studies, a variety of cationic agents with amino, ammonium, sulfonium, phosphonium and other groups have been employed to modify cellulose fabrics, the high cost, the fabric yellowing and toxicity of these substances have prevented their industrial applications. The 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) is a reasonably cheap, reactive and low-toxic chemical which is probably a good cationic agent for the modification of cellulosic fibers [12]. In short, the focus of this article is to investigate the dyeing behaviour of cationized and non-cationized cotton with *Vitis vinifera* L. leaves aqueous extract.

MATERIALS AND METHODS

Experimental

***Vitis vinifera* L. Leaves Identification:** The *Vitis vinifera* L. Black Grenache leaves were collected from "Bir BouRagueba", a suburb in the city of Nabeul, Tunisia. Bir BouRagueba's latitude is 10°25' and its longitude is 36° 37'W. Leaves were lyophilised and reduced to fine powder.

Characterization of the Cotton Fabrics: A bleached plain-cotton fabric of which its weight mass per unit area of 150g.m^{-2} was procured commercially. Before dyeing, the fabric was treated with a solution containing 5 g. L^{-1} non-ionic detergent, at 50°C for 30 min. Then, the fabric was thoroughly rinsed with water and air dried at room temperature.

Cationisation of Cotton with CHPTAC: Desized, scoured and bleached plain woven cotton fabric was used in this work. The cationic agent (CHPTAC) 3-chloro-2-hydroxypropyl trimethyl ammonium chloride is commercially available as a 65% aqueous solution and was purchased from Fluka. Reagent-grade NaOH crystals and Hydrochloric acid (HCl) were purchased from Fluka. Distilled water was used throughout the experiments.

Fourier Transform Infrared Spectroscopic Analysis: Fourier-transform infrared (FTIR) spectra were recorded on a Nexus 470 FTIR Spectrometer, Nicolet Company, USA using potassium bromide disks. A total of 32 scans for each sample were taken with a resolution of 4 cm^{-1}, with a range of 4000–400 cm^{-1}.

The Dyeing Process: Dyeing was performed by the exhaustion method using a liquor ratio of 20:1, with the dye bath being maintained at a different pH (2–7). The pH values were recorded with Eutech pH-meter instruments and adjusted with acetic acids and dilute solution of sodium hydroxide 0.1N. The temperature was raised to 95°C over 30 min and held at this level for 90 min. The dyeing was carried out in the laboratory dyeing machine (Ahiba Datacolour International, USA). Then, the dyed fabrics were removed, rinsed with water, followed by a soaping step using 3 g.L^{-1} of a non-ionic detergent at 60°C during 5 min. Finally, the fabric samples were washed thoroughly with cold water, squeezed and dried at room temperature. The dyeing experiment was performed in duplicate.

Evaluation of Dyeing Quality: The reflectance and the L, a*, b* values of the dyed samples were measured with a Spectro Flash SF300 spectrophotometer (illuminant D65/10o observer) with data

Master 23 software (Datacolor International, USA). Relative color strengths (K/S values) were determined using the Kubelk and Munk equations.

$$\frac{K_{\lambda c}}{S_{\lambda}} = \frac{(1-R_{\lambda})^2}{2R_{\lambda}} - \frac{(1-R_{\lambda t})^2}{2R_{\lambda t}}$$

where R is the decimal fraction of the reflectance of dyed fabric, R_0 is the decimal fraction of the reflectance of undyed fabric, K is the absorption coefficient and S is the scattering coefficient.

L* is corresponding to the brightness (100=white, 0=black),

a* is corresponding to the red/green coordinate (positive sign=red, negative sign=green) and b* is corresponding to the yellow/blue coordinate (positive sign=yellow, negative sign=blue).

Fastnesses Testing: The dyed samples were evaluated according to NF and ISO standard methods: ISO 105-X12: 2002 for color fastness to rubbing; ISO 105-C10:2006 for color fastness to washing and ISO 105-B02:1994 for color fastness to light.

Quantity of Anthocyanins in *Vitis vinifera* L. (Black Grenache) Leaves by Spectrophotometric Method*:* A weighted amount of plant material was extracted with distilled water in a beaker. In the standard procedure, the mass of plant material/volume of liquid ratio was set at 1:20, i.e. 1g of *Vitis vinifera* L. was extracted with 20 ml of water. The extraction was performed for approximately 60 min at 95ºC. The amount of extracted coloured substances as a function of time was monitored by photometry. Total anthocyanins content was determined using the pH differential assay of Giusti et Worlstad. Absorbances (A) were measured photometrically in the range 350-700nm using a 10 mm cuvette and CE 202 UV-Visible diode array spectrophotometer. Absorbances at 520 nm and 700 nm in buffers at pH 1 and 4.5 were used to calculate the concentration of dyes as cyaniding-3-glycoside from Eq (1).

$$A = (A_{520nm} - A_{700nm})\text{pH } 1.0 - (A_{520nm} - A_{700nm})\text{pH } 4.5 \quad (1)$$

Monomeric anthocyanin pigment concentration in the extract was then calculated according to Eqn (2).

$$\text{ACY} = \frac{A \times MW \times DF \times 10^3}{\varepsilon \times l} \quad (2)$$

The determined concentration can be transformed into dye content (DC) in the plant material by multiplication by a factor 20 (1 g of material extracted in 20 ml of water).

Here ACY is the momomeric anthocyanin pigment concentration calculated as mg cyaniding-3-glycoside L^{-1} extract, MW is the molecular weight of cyandin-3-glycoside (449.2 g mol^{-1}), ε= 26,900 molar extinction coefficient, in $Lmol^{-1}cm^{-1}$, for cyd-3-glu; and 10^3 = factor for conversion from g to mg. DF = dilution factor established in D; l = path length in cm[13]

RESULTS AND DISCUSSION

The anthocyanins concentration calculated, with *Spectrophotometric Method,* in the 20 ml of extract is 191mg L^{-1} which is equal to 3.82mg of 1 g of dry *Vitis vinifera* L. leaves which correlated with HPLC analysis results investigated in one of our studies [14].

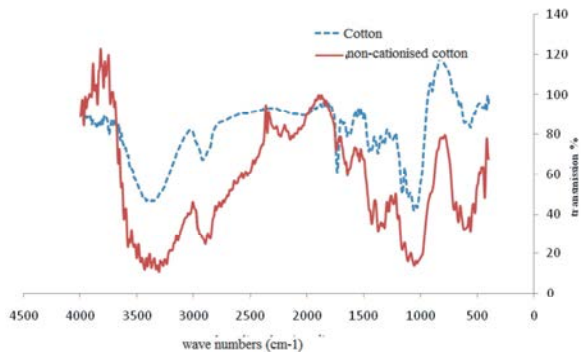

Fig. 2: FTIR spectra the untreated (A) and treated (B); cotton fabric with cationizing agent CHPTAC

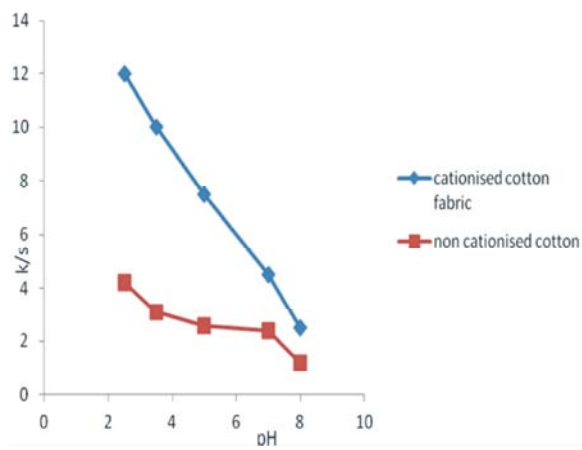

Fig. 3: Effect of dye bath pH on the colour strength of cationised and non cationised cotton fabrics dyed at 95°C

FTIR Analysis: FTIR spectra the untreated (A) and treated (B) (Figure 2); cotton fabric with cationizing Agent, are shown in Fig. 3. The treated cotton fabric (curve B) shows four absorption bands at 2918.79, 2850.04, 1430.17 and 1373.02 cm-1 corresponding to the aliphatic C–H stretching. A broad absorption band with low intensity of the primary –OH stretching band of untreated cotton fabric at 3352.38 cm-1 and 1032.71 cm-1 is observed in spectrum (A). Furthermore, the absorption intensity of primary –OH stretching narrow band at 3343.61 cm-1 which is associated with a band at 1033.05 cm-1 is considerably increased in case of the cationized fabric relative to the untreated cotton fabric. The treated samples showed a characteristic peak at 1199.67 cm-1 due to C–N stretching vibration.

Figure 3 shows that the pH values of the dye bath have a considerable effect on the dyeability of cationized and non-cationized cotton fabrics with *Vitis vinifera* L.

Table 1: Effect of the dyeing temperature on L, a*, b* and depth of shades values (K/S) of dyed cationised and non cationised cotton fabrics dyed with *Vitis Vinifera* L. leaves extract

	a*		b*		L		K/S	
Temperatures	CC	NCC	CC	NCC	CC	NCC	CC	NCC
45	21	1.34	12	6.51	60	87.34	5.6	1.8
60	17.5	2.44	18.2	6.48	55	85.86	6.7	2.6
75	15.8	4.25	20	13.04	47	81.39	7.7	3.3
80	15.2	2.18	20.5	14.71	43.5	76.02	10.6	3.7
95	14	0.84	22	19.01	42	75.02	12	4

CC: cationised cotton; NCC: Non-cationised Cotton.

Table 2: Values of light, wash and rubbing fastness of dyed cationised and non-cationised cotton fabrics, at T= 95°C

	Wash fastness							Rubbing fastness	
	Acétate	Cotton	Nylon	PES	PAC	wool	Light fastness	D*	W*
Non-cationised cotton fabric	5	5	5	5	5	3/4	2	4	¾
Cationised cotton fabric	5	5	5	5	5	5	6	4	¾

Table 3: Colour value of dyed cationised and non-cationised cotton fabrics

Samples	L	a*	b*	k/s
Non-cationised cotton fabric	75	0,84	19	4,1
Cationised cotton fabric	42	14	22	123

extract. It is clear that cationisation has improved the dyeability of the fabrics at pH 2 and 2.5 values. The acidic pH dye bath enhances the dyeability of cotton fabric especially cationized one with *Vitis vinifera* L. extract. The effect of dye bath pH can be attributed to the correlation between dye structure and cationized cotton fiber. Since the *Vitis vinifera* L. leaves extract contains anthocyanins which are water-soluble dyes containing many hydroxyl groups, it would interact ionically with the protonated terminal amino groups of cationized cotton fibers at acidic pH via ion exchange reaction. Thus, these kinds of interactions take place together with ionic forces. This ionic attraction would increase the dyeability of the fiber as clearly shown in Figure 3.

Effect of Temperature: As it is well recognized, the dye bath temperature plays an important role in dyeing with natural dyes. A case in point, the stability of the anthocyanin pigments largely depends on temperature among other factors [13]. We notice for both cationized and non cationized cotton fabric that: Table 1 shows the effect of the temperature of dyeing on L*, a*, b*, ho, C* and K/S values. When dyeing temperature increased, the values of L* decreased and the values of K/S increased. Thus, the highest value of L* and lowest value of K/S showed lighter shades, while both the lowest values of L* and the highest values of K/S signify deeper shades of dyed samples. Positive a* and positive b* represent red and yellow, respectively. Therefore, samples dyed at 45° C have higher value of a* than those dyed at 95° C. These results correlate with red and brown shades of dyed fabrics, which could be explained by the temperature effect on anthocyanins. As it expected, the dye-up take of cationized-cotton fabrics is better than non-cationized ones which is may be due to, first, the fiber swelling effects that enhance the dye diffusion. Second, it can be attributed to the correlation between the dye structure and cationized cotton fibers. Since the anthocyanins act as an acid dye, it would interact ionically with the protonated terminal amino groups of the cationized cotton fibers under acidic medium (pH 4) via electrostatic dye attraction.

Fastness Properties: The light, wash and rubbing fastness values of cationized and non cationized cotton fabrics dyed with *Vitis vinifera* L. leaves aqueous extract are shown in Table 2. The control sample shows good rubbing and wash fastness properties of cationized dyed fabrics (3/4-5 units on the grey scale whereas 5 is the higher rating). This result can be explained by the affinity of cationized cotton fiber to anthocyanins. The light fastness of cationized cotton fabrics is good (6 units on the standard blue scale whereas 8 is the highest rating) which is better than those obtained with non cationized cotton fabric. The cationized cotton fabric dyed with *Vitis vinifera* L. leaves extract shows higher colour strength than the non-cationized cotton fabric because cationized cotton fabric contains more functional groups than the

non-cationized one. In fact, the cationisation of cotton fabrics enhances the good penetration of the colour in the fiber matrix. The value results obtained (Table 3) illustrate that non-cationized cotton shows a yellowish-brown colour; however, cationized cotton fabric shows redish-brown colour. It can be concluded that cationized cotton fabrics can be successfully dyed with *Vitis vinifer* L. leaves extract. Anthocyanins contain phenolic compounds. The anionically charged phenolic groups could form an ionic bond with cationics (amino groups) in the cationic cotton fabric.

CONCLUSION

The cationization of cotton fabrics, dyed with *Vitis vinifera* L. leaves aqueous extract, in addition to its asset of saving processing time and energy, it also helps to obtain higher dye-uptake as well as good fastness dyeing properties.

REFERENCES

1. Adeel, S., Ali, S. Bhatti and F. Zsila, 2009. Dyeing of cotton fabric using pomegranate (*Punica granatum*) aqueous extract. Asian J. Chem., 21: 3493-3496.
2. Bombardelli, E. and P. Morazzonni, 1995. *Vitis vinifera* L. Fitoterapia, 66: 291-294.
3. Hmamouchi, M., M. Lahlou, N. Es-Safi and A. Agoumi, 1998. Molluscicidal properties of some proanthocyanidins, flavones and flavonols. Fitoterapia, 69: 161-165.
4. Felicio, J., R. Santos and E. Gonçalez, 2001. Chemical constituents from *Vitis vinifera* L. (Vitaceae). Arq Inst Biol., 68: 47-50.
5. Monagas, M., M.I. Garrido, B. Bartolomé and C. Gómez-Cordovés, 2004. Chemical characterization of commercial dietary ingredients from *Vitis vinifera* L. Anal Chim Acta, 563: 401-404.
6. Izabela, K. and Z. Wei, 2004. Anthocyanins-More Than Nature's Colours. J. Biomed Biotechnol., 5: 239-242.
7. Burkinshaw, M. and A. Gotsopoulos, 1996. Pretreatment of cotton to enhance its dyeability; Part 2. Direct dyes. Dyes Pigments, 32: 209-2012.
8. Chen, W., S. Zhao and X. Wang, 2004. Improving the Color Yield of Ink-Jet Printing on Cationized Cotton, Text Res J., 74: 68-71.
9. Kim, Y. and G. Sun, 2002. Functional finishing of acrylic and cationic dyeable fabrics Intermolecular Interactions. Text Res J., 72: 1052-1055.
10. Wu, M. and S. Kuga, 2006. Cationization of cellulose fabrics by polyallylamine binding. J. Appl. Polym. Sci., 100: 1668-1671.
11. Rong, L. and G. Feng, 2006. Dyeing properties of PECH-amine cationized cotton with acid dyes. J. Appl. Polym Sci., 100: 3302-3305.
12. Liu, Z.Y., Yang, L. Zhang, Z. Liu and H. Xiong, 2007. Study on the cationic modification and dyeing of ramie fiber. Cellulose, 14: 337-340.
13. Lee, G., D. Robert, E. Ronalad, K. Barnes, T. Eisele and M. Giusti, 2005. Determination of Total Monomeric Anthocyanin Pigment Content of Fruit Juices, Beverages, Natural Colorants and Wines by the pH Differential Method: collaborative study. J. AOAC Int., 88: 1269-1272.
14. Rym, M., E. Bechir and M. Farouk, 2013. Dyeing properties of wool fabrics dyed with *Vitis vinifera* L. (black grenache) leaves extract. Fiber Polym., 14: 786-789.