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A Challenging Approach to Improve the Low Affinity of Acrylic Fibres to Be Successfully Dyed with a Bio-Colorant Extracted from Grape Marc

Noureddine Baaka[1,*], Manel Ben Ticha[1, 2], Wafa Haddar[1, 3] and Mohamed Farouk Mhenni[1]

[1]University of Monastir, Faculty of Sciences of Monastir, Research Unity of Applied Chemistry and Environment, 5000 Monastir, Tunisia.

[2]National Engineering School of Monastir, 5019 Monastir, Tunisia.

[3]Higher Institute of Technological Studies, 5070, Ksar Hellal, Monastir, Tunisia.

[*]Correspondence Author: Noureddine Baaka. Email: nouri.baaka@gmail.com.

Abstract: Acrylic fibres are highly crystalline and non-polar polymers, which makes their dyeing a very difficult step that poses real technical challenges. In order to overcome this concern, it is intended in this paper to modify acrylic fibers by different methods namely cationisation using the Crosscolor DRT then amidoximation using hydroxylamine hydrochloride and ammonium acetate. The resulted samples were dyed then with the bio-colorant extracted from grape marc. The effect of the pretreatment on fibers fine structure using X-ray diffraction and the scanning electron microscope (SEM) images and its correlation with the colour strength of the dyed fabrics was investigated. The dyeing parameters, such as dye bath pH and temperature on the performances of this dyeing process were studied. Good dyeing qualities and new shades varying from brown to grey and dark green have been obtained following process optimization, mordanting and modification of acrylic fibers by the technique of cationisation.

Keywords: Modified acrylic fibers; grape marc; bio-colorant; mordant.

1 Introduction

The management of agricultural by-products has become a major problem for the food industries due to their excess generation and limited exploitation. *Vitis vinifera L.*, also known as grape, is considered as the second world's largest fruit. About 80% of the total production is mainly used for the production of wine [1]. Winemaking is one of the most important agricultural sector contributing substantially to national economies around the world. Total worldwide wine production is around 260 million hL, 60% of which is produced by European Union countries. Winemaking generates huge quantities of by-products. Grape pomace, the main winemaking by-product, is a solid residue consisting of skins, pulp, stalks, and seeds [2] which account for 25-35 Kg/hL of produced wine. Due to the environmental concerns and potential profitable applications, the use of wine by products is gaining increasing attentiveness [3,4].

Grape pomace contain several classes of polyphenolic compounds. This term mainly includes anthocyanins, flavanols, flavonols, and phenolic acids [5].

In recent years, both researchers, practitioners and consumers have devoted attention to environmental and socio-economic sustainability issues in the textile industry [6]. In textile industry, there has been a growing tendency towards the use of natural dyes in the textile field due to the increasing consciousness of ecology, sustainability and environment. Nevertheless, the utilization of these dyes has remained modest due to the high costs and low availability. Thus, scientists were conducted to find out new sources of natural colouring agents and especially from industrial by-products [7-10]. Scientists working in the field of natural colourant technology are now focusing to improve extraction of colourant from natural sources. Various techniques were used. Researchers have using microwave and ultrasonic techniques to to improve the extraction of colourant from plants [11-13].

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Acrylic fibre is one of the most popular synthetic fibres and has replaced wool in many respects. The fibre has many applications in apparel, as well as in related industrial sectors, due to its outstanding physical and chemical properties, such as high strength. However, high hydrophobicity and the low dye affinity hoop this fibre from being efficiently used in the textile industries.

Different techniques such as chemical modification to include amidoxime groups on polymer surface [14,15] and cationization [8,16,17] were used to improve the dyeing performances of fibres.

The present work exhibits a viable and efficient method for acrylic fibre pretreatment to render it more hydrophilic and thus dyeable with natural dyes extracted from grape pomace. The chemical modification of acrylic fibres was performed in order to enhance the dyeability of this fibre by grape pomace natural dyes. The effect of the pretreatment on fibre fine structure using X-ray diffraction and the scanning electron microscope (SEM) images and its correlation with the colour strength of the dyed fabrics is investigated. The effect of mordanting on dyeing of modified acrylic by grape pomace natural matters was also studied.

2 Experimental

2.1 Materials and Chemicals

Grape pomace was obtained by winemaker in Northern Tunisia, in 2015. They were a mixture of several grape varieties. Subsequently the dried material was ground and a fine powder was obtained.

Acrylic fabric (Plain weave and weight, 200 g/m) was procured commercially. Before being used, it was soaped with 2 g/L of non-ionic detergent at 60°C for 30 min, thoroughly rinsed and air-dried.

Alum ($KAl(SO_4)_2 \cdot 12H_2O$, Fluka), stannous chloride ($SnCl_2$, Sigma Aldrich), copper sulphate hydrate ($CuSO_4 \cdot 5H_2O$, Fluka) and ferrous sulphate ($FeSO_4 \cdot 7H_2O$, Riedel-de-Haen), sodium chloride (NaCl, Chimi-pharma), hydroxylamine hydrochloride (H_3NO. HCl, Sigma Aldrich) ammonium acetate ($C_2H_7NO_2$, ShamLab), Croscolor DRT (Eurodye-CTC) were laboratory reagents grade and were used without further purification.

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

The CIE L*, a*, b* and colour yield (K/S) values of dyed samples were measured using a spectrophotometer with data Master 2.3 (Datacolor International, USA) with illuminant D65 at 10 degree observer.

2.2 Instruments

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2.3 Acrylic Modification

Pretreatment 1: amidoximation

Following a previously described method, a known weight of acrylic fibres was pretreated with different concentrations of hydroxylamine hydrochloride (0, 2, 6, 10, 20 and 30 g/L) using aqueous solutions of ammonium acetate (0, 6, 9, 15, 30, 60 g/L) at a liquor ratio of 40:1 , at a temperature of 85°C for 60 min.

Pretreatment 2: cationization

The proposed method consists of treating acrylic before the step of dyeing with different amounts of a cationizing agent (Croscolor DRT) during 60 min at 50°C. After that, acrylic was dried.

2.4 Extraction

The extraction method was followed according to the optimum condition reported previously [18]. The plant materials (7 g) were soaked in water (100 mL) in presence of sodium hydroxide concentration of about 0.13 M and then the coloring was extracted at 80°C for 70 min. The obtained extract was separated by filtration and used for dyeing.

2.5 Dyeing Process

Acrylic fibres were dyed in a dye bath containing aqueous extract of grape pomace with liquor ratio 40:1. The dyeing was carried out at different pH values (2-9), for different durations (15-100 min), at different temperatures (30-100°C) and in the presence of different salt concentration (0-25 g/L). After dyeing, the samples were rinsed and dried.

2.6 Mordanting Processes

Pre-mordanting, meta-mordanting and post-mordanting methods were used in this study. Aluminium sulphate hydrate (alum), ferrous sulphate and copper sulphate were used with a concentration of 3% (w/w with respect to the fabric).

In the pre-mordanting method, acrylic fabrics were first treated with mordant for 45 min at 30°C. After that, mordanted fabrics were dyed.

In the case of meta-mordanting technique, the fabrics were immersed in a bath containing the dye solution and a mordant. The dye conditions are pH 3, 100°C and 60 min. Acrylic fabrics were rinsed, soaped with Cotoblanc RS at 60°C, washed and dried.

For post-mordanting method, fabrics were dyed in the absence of a mordant, followed by mordanting in a separate bath containing a mordant.

2.7 Evaluation of Colour Strength and Fastness Properties

The colorimetric properties of dyed acrylic samples were obtained in terms of CIELab values (L*, a*, b*) and colour strength (K/S). The colour strength (K/S) in visible region of the spectrum (400-700) was calculated based on Kubelka-Munk equation [19]:

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

where (K) is the adsorption coefficient, (S) is the reflectance of dyed sample and (R) is the reflectance of dyed sample.

The dyeing qualities of the mordanted dyed samples were evaluated by measuring the Sum (K/S) as follow [8]:

$$Sum(K/S) = \sum_{\lambda=400}^{700} (K/S)_\lambda \tag{2}$$

Total colour difference of dyed woolen yarn samples were obtained using following relationships:

$$\text{Colour Difference } (\Delta E) = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \tag{3}$$

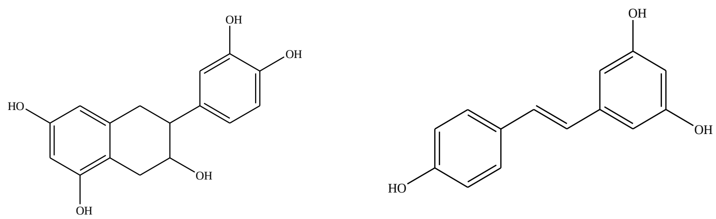
where ΔL = L*mordanted - L*unmordanted; Δa = a*mordanted - a*unmordanted; Δb = b*mordanted - b*unmordanted, ‘L’ describes lightness, ‘a’ measures redness or greenness; and ‘b’ means the degree of yellowness or blueness.

2.8 X-Ray Diffraction

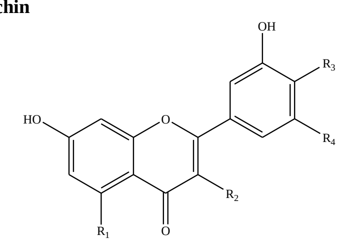
X-ray diffraction analysis was performed at room temperature for the untreated and treated acrylic fibres on an X-ray diffractometer model Philips X Pert MPP with a type PW 3050/10 goniometer (USA).

2.9 Scanning Electron Microscope

The unmodified and modified acrylic fibres were examinated using a SEM HITACHI S-2360. The acceleration voltage of work was between 8 and 22 kV [20].

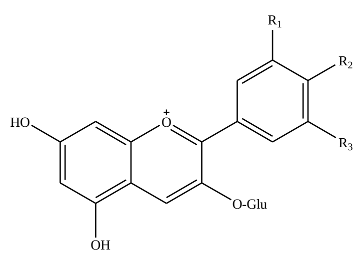


Catechin **Resveratrol**



Flavonols

	R1	*R2*	*R3*	*R4*
Quercetin	OH	OH	OH	-
Rutin	OH	O-Rutinose	OH	-
Morin	OH	OH	-	OH
Myrecitin	OH	OH	OH	OH
Fisetin	OH	OH	OH	-



Antocyanins

	R1	*R2*	*R3*
Peonidin-3-O-glucoside	OCH_3	OH	-
Petunidin-3-O-glycoside	OH	OH	OCH_3
Malvidin-3-O-glucoside	OCH_3	OH	OCH_3
Cyanidin-3-O-glucoside	OH	OH	-
Dephinidin-3-O-glycoside	OH	OH	OH

Figure 1: The chemical structures of some phenolic compounds found in grapes pomace

3 Results and Discussion

3.1 Modification of Acrylic Fibres

Effect of the cationizing agent amount

The effect of acrylic treatment with croscolor DRT, as cationizing agent, on the colour yield of dyed fabrics was shown in Fig. 2. The amount of the cationizing agent was varied from 0 to 17.5% (w/w with respect to the fabric).

This figure clearly indicates that modifying acrylic enhanced its dyeability by the aqueous extract of grape pomace. Initially, the acrylic fibres have a low affinity to the grape pomace aqueous extract (K/S = 1.5). However, when acrylic is treated by cationizing agent, its affinity raised and attain a value of K/S equal to 7.8.

This figure shows, also, a bend composed of two parts: in the first one, a speedy increase of the colour yield was shown until using 10% of the cationizing agent. The improvement of the dyeing quality is due to the rise of the number of quaternary ammonium groups in acrylic fibres, which provokes an increase of the absorption rate of the natural dyes by acrylic. In the second part of the bend, the colour yield was maintained stable. This could be attributed to the saturation of the acrylic fabric with colorant.

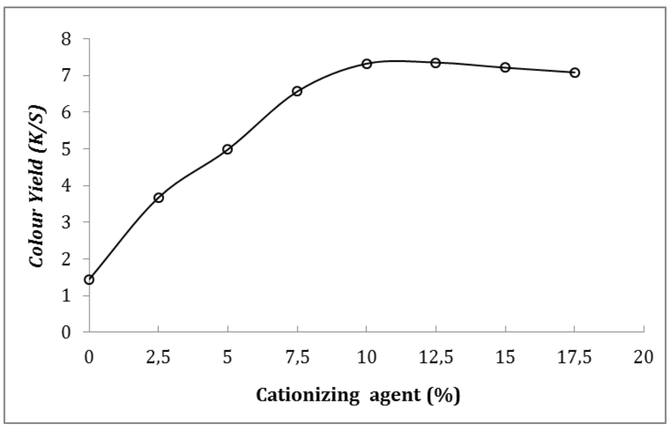


Figure 2: Effect of the cationizing agent amount on the colour yield (K/S)

Amidoximation: Effect of Hydroxylamine Hydrochloride; ammonium acetate combination

Preliminary tests show that the acrylic fibres does not exhibit a high affinity for the colouring compound extracted from grape pomace. To enhance the dyeability of acrylic fibres with grape pomace aqueous extract, an amidoximation method was proposed. This modification consists of converting some of the nitrile groups present in the fibres macromolecules into amino groups. The presence of these groups could return acrylic fibres more hydrophilic, less crystalline and more dyeable by the phenolic groups of grape pomace extract [21]. The modified acrylic fabrics were then dyed with grape pomace aqueous extract. Fig. 3 shows the effect of the hydroxylamine hydrochloride and the ammonium acetate combination on the colour yield of the dyed fabrics. This figure point that the colour yield increases with the increase of hydroxylamine hydrochloride and ammonium acetate concentrations. The colour yield (K/S) reaches its maximum at a concentration of 10 g/L hydroxylamine hydrochloride and 15 g/L of ammonium acetate with a value of K/S equal to 7.87, which is a dyeing quality to close to that obtained by cationizing the acrylic fibres.

The results presented in Fig. 3 could be explained by the fact that the fibre becomes saturated with dyes compounds and thus further dye penetration would be hampered due not only to the blocking effect imposed by the pre-exhausted dye molecules, but also the high compactness of the pretreated fibres at concentrations of hydroxylamine hydrochloride up 10 g/L [21].

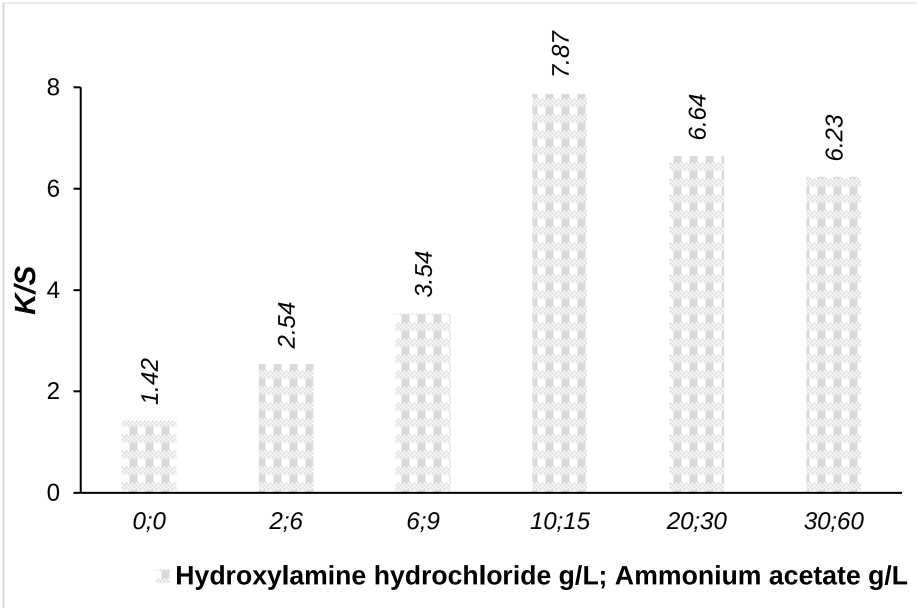


Figure 3: Effect of the hydroxylamine hydrochloride and ammonium acetate concentrations, on the colour yield (K/S) of dyed modified acrylic fabrics

3.2 Characterization of the Acrylic Fibres

X-ray diffraction

Fig. 4 shows X-ray diffraction patterns for the untreated and modified acrylic fibres (cationized and amidoximated) are presented in Fig. 4. The untreated acrylic showed one intensive peak at $2\theta \cong 17°$ and other peak of low intensity at $2\theta \cong 30°$ [22]. Compared to the blank sample, the two modified samples show a less intensive and more broader peak at $2\theta \cong 17°$. The decline of intensity indicates a possible reduction in the crystallinity. While the broadering represents a reduction in crystal size [23]. Consequently, it could be deduced the colour yield could be increase via cationizing then via amidoximation of the acrylic fibres.

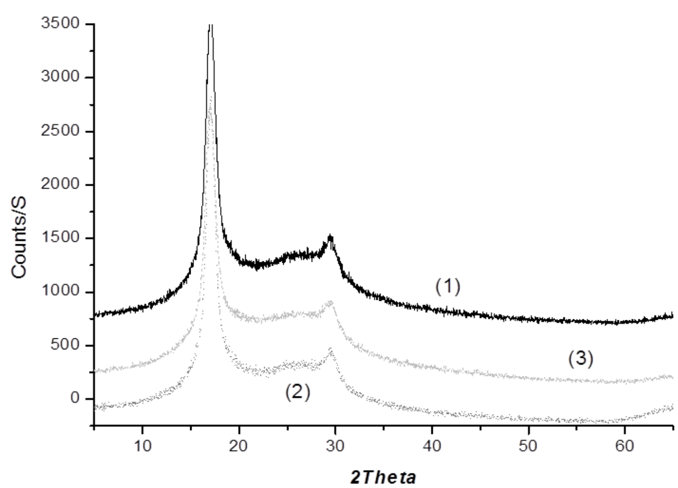


Figure 4: X-Ray Analysis of untreated acrylic (1), cationized acrylic by Croscolor DRT (2) and amidoximated (3) fabrics

Morphological study

To investigate the surface structure of solids, the scanning electron microscope (SEM) is usually used [24]. In this study, the acrylic fibre s surface structure was examined by scanning electron microscopy in order to estimate the acrylic modification on surface morphology.

The obtained are presented in Fig. 5. Based on this graph, it could be observed that the surface of the modified fibre s was a little rougher compared with that of the untreated one [20].

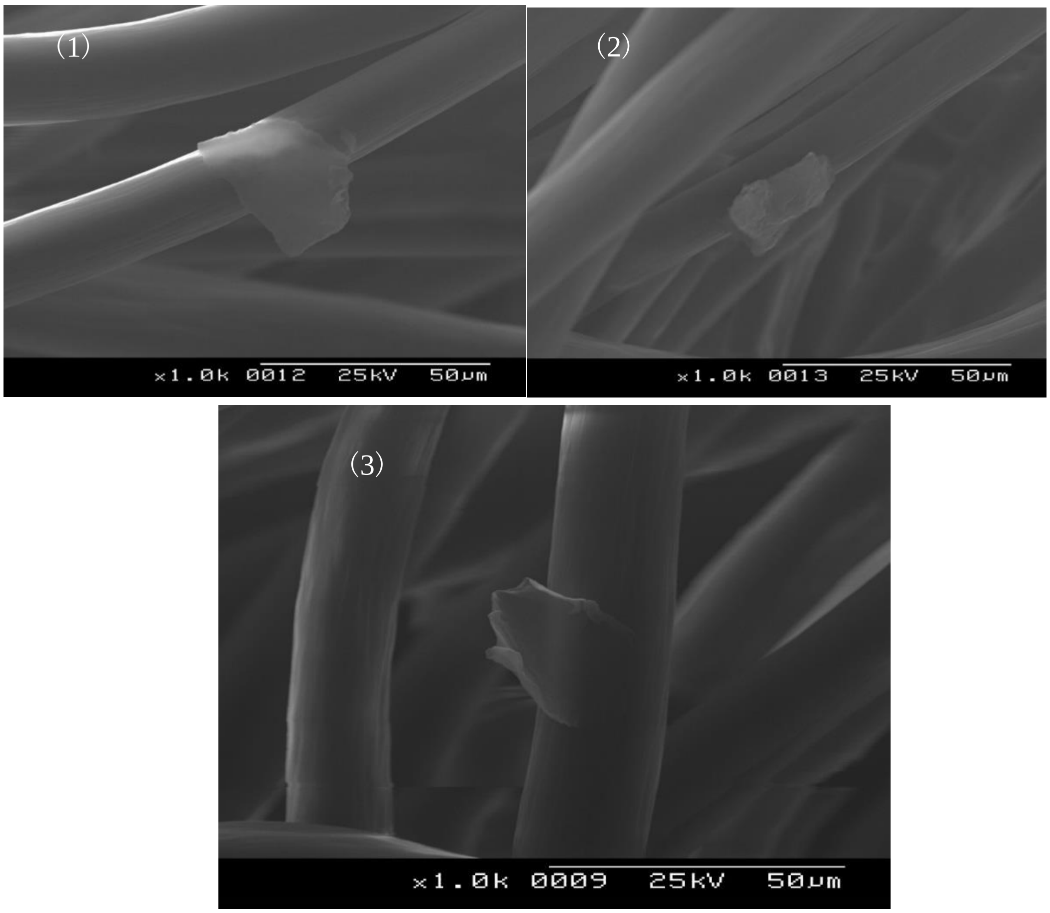


Figure 5: SEM photographs of untreated fibres (1), cationized acrylic fibres (2) and amidoximated acrylic fibres (3)

3.3 Dyeing of Modified Acrylic Samples

Two modified acrylic samples A (cationized by 10% of Croscolor DRT) and B (amidoximated with 10 g/L of hydroxylamine hydrochloride and 20 g/L ammonium acetate) were dyed with grape pomace aqueous extract. Thus, comparative studies for the dyeability of the samples as well as the factors that could affect the dyeing processes were studied.

Effect of the dye bath pH

Generally, natural and synthetic dyes have a colour which depends on the pH of the medium in which they are in solution. This parameter has an influence on the course of the process for dyeing textile fibres. Therefore, the pH effect on the dyeing quality of modified acrylic fabrics was studied. The obtained results illustrated in Fig. 6 showed that, up to the value 3, the colour yield (K/S) gradually decreases (at pH = 9, K/S = 2.21 for the case of cationised acrylic and K/S = 1.92 for the case of amidoximated acrylic). These results signify that the best result is obtained in acid medium. The decrease in colour yield with the increasing of the dye bath pH can be explained by the correlation between dye molecules and acrylic fibres. Thus, acid medium is expected to reduce the negative charge of the surface of acrylic fabrics in the dye bath and as a consequence the dyeability increases [21].

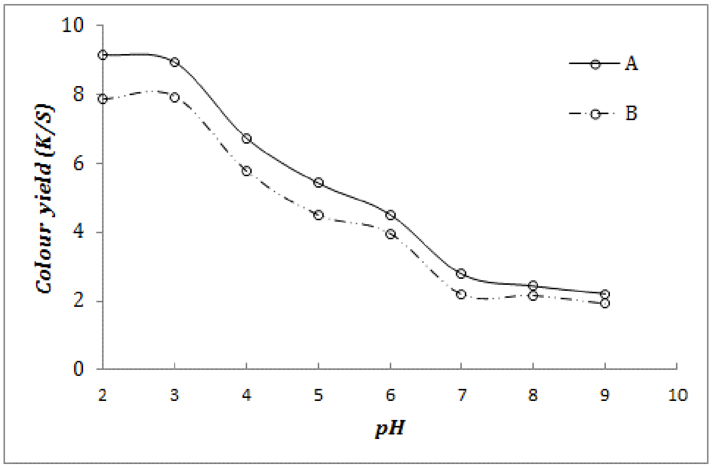


Figure 6: Effect of the dye bath pH on the colour yield (K/S) for cationized (A) and amidoximated (B) acrylic fibers

Effect of temperature

The effect of temperature on the dyeability of acrylic fabrics with grape pomace aqueous extract is shown in Fig. 7. This figure clearly indicates that the colour yield values increase with the dyeing temperature for the two samples. The cationised sample (A) revealed higher colour yield values at all temperatures compared with those of amidoximed sample (B). Indeed, by increasing the temperature, the migration of dye molecules in the fibre is promoted, due to the decrease of surface tension and swelling of the fibre. Therefore, the mobility of the dye molecules and their migration into the fibre was favorated [25].

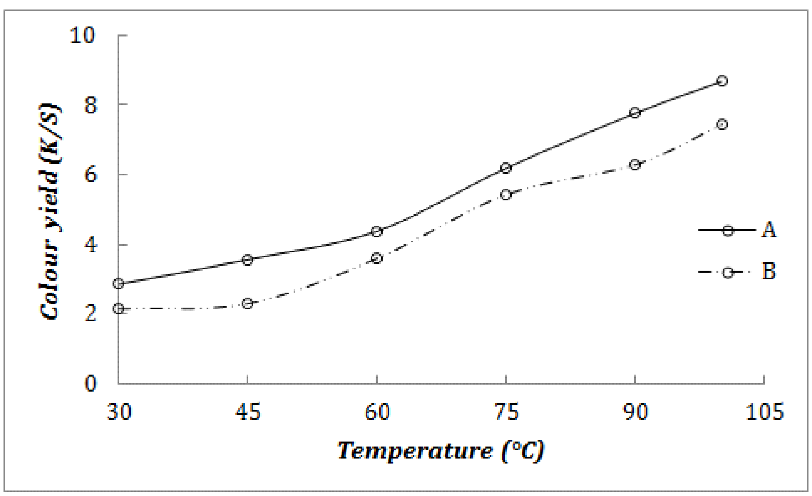


Figure 7: Effect of the dye bath temperature on the colour yield (K/S) for cationized (A) and amidoximated (B) acrylic fibers

Effect of dyeing time

The effect of the dyeing duration on the colour yield (K/S) of modified acrylic fabrics is shown in Fig. 8. Based on this figure, it can be noted that colour yield increases with the increasing of dyeing time until dye exhaustion attains equilibrium. At this stage, there is a decline in the colour yield after further increase in time from 60 minutes (at 60 minutes the K/S = 8.63 for cationized acrylic and K/S = 6.96 for amidoximed acrylic). It can be noticed, also, that the cationised sample (A) revealed higher colour yield values at all duration time when compared with those of amidoximed sample (B).

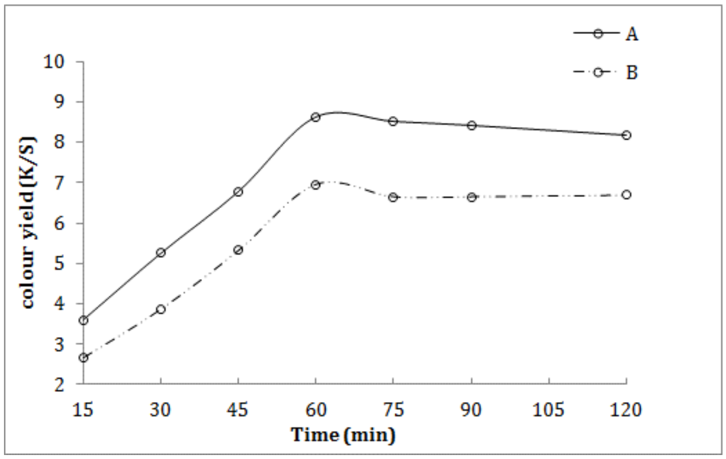


Figure 8: Effect of the dyeing time on the colour yield (K/S) for cationized (A) and amidoximated (B) acrylic fibers

Effect of salt concentration

Fig. 9 shows the effect of salt concentration on the colour yield obtained for the dyed fabrics. This figure clearly indicates that the colour yield decreases as the salt concentration increases. This could be explicated by the retarding effect of the electrolyte on the rate of dye absorption [26]. Thus, dyeing without salt addition is the best dyeing condition.

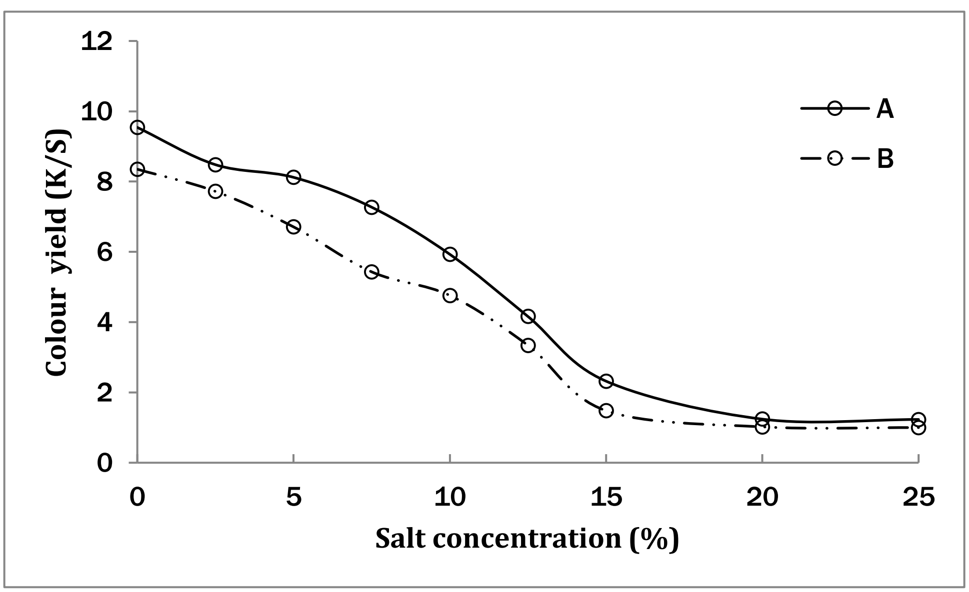


Figure 9: Effect of the salt concentration on the colour yield (K/S) for cationized (A) and amidoximated (B) acrylic fibers

3.4 Effect of Mordanting Treatments

Effect of the mordanting conditions on dyeing properties

Pre-mordanting, meta-mordanting and past-mordanting methods were used for dyeing acrylic fabrics cationised with 10% of Croscolor DRT. Tab. 1 shows the ∑ K/S, a*, *b, L*, the total colour difference (ΔE) and the obtained shades of the dyed fabrics with and without mordanting. Results indicated that the colorimetric parameters values (L*, a* and b*) have been changed by the addition of the mordants. During the dyeing of acrylic with grape pomace aqueous extract, dark brownish shades were generally obtained. With ferrous sulphate, brownish black and brownish green shades were obtained.

Tab. 1 shows that in the case of pre-mordanting method, copper sulphate gave higher colour yield (∑ K/S = 160.58). The (∑ K/S) values of the dyed fabrics are classified to the following increasing order:

Alum > without mordant > ferrous sulphate > Copper sulphate

From Tab. 1, it could be seen that, in the case of meta-mordanting method, highest colour yield and highest total colour difference are obtained for all used mordants. It can be noted, also, that copper sulphate and ferrous sulphate are the best mordants. Thus, these two mordants are well known for their ability to form coordination complexes with the dye [27].

It can be observed in Tab 1 that, in the case of post-mordanting method, ferrous sulphate gave the highest colour yield (∑ K/S = 146.34), and the highest total colour difference (ΔE = 16.16). The (∑ K/S) values of the dyed fabrics increased in the following order:

Without mordant > Copper sulphate > Alum > Ferrous sulphate

Effect of the mordanting conditions on fastness properties of dyed fabrics

The rating of fastness (washing, rubbing and light fastness) of unmordanted and mordanted acrylic fabrics are shown in Tab. 2. It was found that the fastness of unmordanted fabrics are considerably good except light fastness which was medium (noted 3 per 8 graduations of the blue scale). Generally, it is well known that the poor light fastness was a problem for natural dyes.

Tab. 2 shows that mordanting methods improved almost of the fastness properties of the dyed fabrics with grape pomace aqueous extract. The good values of fastness properties could be explained by the fact that the aqueous extract of grape pomace is rich with phenolic compounds (tannins, flavonoids …) which are known to form stable complexes with metal cations. Hence, after mordanting, there is an improving of the fastness properties [28].

Table 1: The dyeing colorimetric data (*L*. a* b**) for the dyed samples with and without metallic salts in the case of acrylic fabrics cationized with 10% Croscolor DRT

Method	**Mordant**	**Shades**	**∑ K/S**	**L***	**a***	**b***	**ΔE**
Without mordant		Brown	79 .52	52.24	6.36	15.81	-
Pre-mordanting	**Copper sulphate**	Brown	160.58	38.19	6.22	15.21	14.06
	Ferrous sulphate	Brown	146.23	39.74	4.87	11.39	13.34
	Alum	Brown	74.44	54.20	5.35	17.45	2.74
Meta-mordanting	**Copper sulphate**	Brown dark	190.24	37.52	7.21	17.54	14.84
	Ferrous sulphate	Brown dark	184.13	34.94	2.38	6.17	20.20
	Alum	Brown	94.77	51.64	5.71	20.37	4.64

Post-mordanting	**Copper sulphate**	Brown green	92.48	50.27	5.86	17.24	2.48
	Ferrous sulphate	Brown green	146.34	38.84	2.34	7.71	16.16
	Alum	Brown	82.77	51.41	6.41	16.35	0.99

Table 2: Fastness properties of the dyed samples with and without mordant

Method	**Mordant**	**Light**	**Wash**	**Rubbing**	
				Dry	**Wet**
Without mordant		3	4	4	3
Pre-mordanting	**Copper sulphate**	4	4	4-5	3-4
	Ferrous sulphate	5	4	4-5	3-4
	Alum	4	4	4-5	3-4
Meta-mordanting	**Copper sulphate**	4	4	4-5	3
	Ferrous sulphate	4	4/5	4	3
	Alum	4	4/5	4	3
Post-mordanting	**Copper sulphate**	5	4	4-5	4
	Ferrous sulphate	5	4/5	4-5	4
	Alum	4	3	4-5	4

4 Conclusion

In this study, it was established that acrylic modification by cationisation and amidoximation improves the dyeing quality resulted from the aqueous extract of grape pomace and also, leads to good fastness properties without using mordant. Then, It was proven that the cationisation of acrylic is more efficient that its amidoximation to enhance its dyeability. Besides, the fastness properties of the modified dyed samples were improved by the using of mordants. Furthermore, it was found that the best dyeing quality of modified acrylic fabrics was obtained for a dye bath pH of 3, a dyeing duration of 60 min and a dyeing temperature of 100°C without using of salt.

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