

ECO-FRIENDLY DYEING OF MODIFIED COTTON FABRICS USING OLIVE DYES EXTRACTED FROM OLIVE MILL WASTEWATER: FOCUS ON DYEING QUALITIES AND ENVIRONMENTAL PERFORMANCES

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ABSTRACT

Olive dyes extracted from stocked olive mill wastewater (OMW) were successfully adsorbed on several modified cotton fabrics giving brown shades with generally good dyeing fastnesses. The results showed also that modified cottons with Tannic acid (commercial polyphenol compound) and with Croscolor DRT (commercial cationising agent) had high affinity to the colouring matters of the OMW. The maximum colour yields were found at an initial pH of OMW. The use of mordanting processes offered deep shades and enhanced fastness properties, especially in the case of post-mordanting with ferrous sulphate. Besides, it was found that cationised cotton with Croscolor DRT absorbed more polyphenols and reduced more the Biological oxygen demand *BOD*₅ of dyeing bath than modified cotton with Tannic acid. However, modified cotton with Tannic acid reduced more the Chemical oxygen demand *COD* of dyebath.

KEYWORDS

Olive mill wastewater valorisation; olive dyes; modified cotton dyeing; dyeing qualities; environmental performances.

1. INTRODUCTION

Synthetic dyes are more available than natural dyes were in the past, because of lower prices and wider ranges of bright shades with considerably improved colour fastness properties (Broadbent, 2001).

In current years, there is a worldwide return to the use of natural dyes in textile applications due to the increase of the concern for the environment (Kamel et al., 2005; Lee, 2007; Bechtold et al., 2007; Montazer and Parvinzadeh, 2007; Vankar et al., 2008a; Vankar et al., 2009; Shaukat et al., 2009; Ghouila et al., 2012; 2014; Meksi et al., 2012, Haddar et al., 2014a; 2018; Ben Ticha et al., 2016; 2017). Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment. Also, they can show a lower toxicity and allergic reaction than synthetic dyes (Tiwari and Vankar, 2001; Gupta et al., 2001; Bhuyan et al., 2004; Haddar et al., 2014; Ben Ticha et al., 2016; 2017). However, the less availability and the high cost of natural dyes are also associated with the limitation of the application of these dyes in the textile industry. Indeed, their use is mainly limited to the manufacturing of upmarket products and the eco-friendly textiles.

On the other hand, the olive mill wastewater (OMW) is an aqueous effluent generated annually by the olive oil extracted industry. The quantities of this wastewater are enormous especially in the Mediterranean region with up to 30 million m³ of OMW produced every year (Tezcan Un et al., 2008). This

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causes serious ecological problems in these countries because until now there is no efficient technique to treat or valorise this effluent and the most frequent method to reduce its ecological impact is to store it in arranged (Figure 1) or unarranged (Figure 2) evaporation ponds. In spite of their environmental problems, it appears that this industrial wastewater contains huge reserves of natural dyes which are abundant and renewable, but until now are not exploited (Meksi et al., 2012). The olive mill wastewater (OMW) is characterized by dark brown to black colour. It was reported that the major colouring components in OMW are tannins and phenolic compounds (Kallel et al., 2009; Yesilada et al., 1994; Hamdi and Garcia, 1993; Gonzalez et al., 1990). Examples of phenolic compounds present in OMW are: cinnamic acid derivatives such as caffeic acid, benzoic acid derivatives such as protocatechuic acid and tyrosol related compounds such as tyrosol and hydroxytyrosol (Miranda et al., 2001; Ramos-Cormenzana et al., 1996; Vázquez Roncero et al., 1974). OMW also contains flavonoid compounds like apigenin, luteolin and quercetin (Obied et al., 2007; Ramos-Cormenzana et al., 1996). The nature of these phenolic compounds and their corresponding concentrations in OMW depend, among factors, from extraction processes, olive ripening, olive storage duration before milling and OMW storage duration (Annesini and Gironi, 2003).

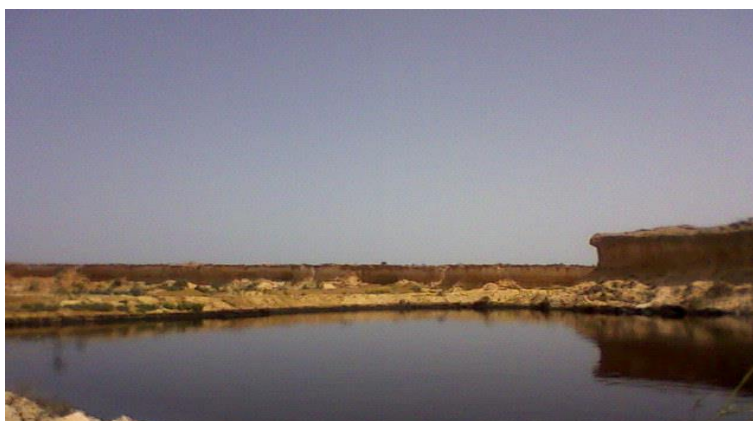


Figure 1: Arranged evaporation pond of olive mill wastewater (OMW)



Figure 2: Unarranged evaporation pond of olive mill wastewater (OMW)

In previous works, it was shown that the OMW could be successfully exploited as a natural dye for dyeing wool fabrics (Meksi et al., 2012) and synthetic fibres (Haddar et al., 2014b; 2015). The developed dyeing approach is very interesting because firstly it contributes to resolving the environmental problem of olive mill wastewater. Then, it provides natural colours on wool and some synthetic fabrics with low costs. In order to make this process more attractive and exhaustive, it is necessary to apply it to other textile fibres and specially cotton which is the most important textile fibre in the world. Cotton possess the majority share (over 50%) among fibres for apparel and textile goods (Gordon and Hsieh; 2007). However, our preliminary dyeing experiments showed that natural dyes from OMW were not able to dye cotton fibres because they had a low affinity to cellulose. To enhance the attraction between this textile fibre and olive

dyes, a route consisting of the cotton modification via pre-treatment using tannins (Vankar et al., 2008a; 2008b; 2009) or cationising agents (Kamel et al., 2009; 2011) could be used.

So, the purpose of this paper is to investigate the valorisation of the olive mill wastewater (OMW) on the dyeing of modified cotton fabrics. The effect of some experimental conditions (the dyebath pH, the dyebath temperature, the dyeing time, the nature and the amount of modifying agent) as well as mordanting conditions on the dyeability of modified cottons with olive dyes were studied. The environmental impact of this dyeing process on the OMW dyebath characteristics (Total polyphenols, Chemical Oxygen Demand COD and Biological Oxygen Demand BOD₅) was also studied.

2. EXPERIMENTAL

2.1. Materials and chemicals used

Commercially bleached but unfinished cotton fabric with the following specifications was supplied from SITEX, Tunisia: plain weave; ends per inch, 33.02; picks per inch, 38.1; warp count, 10.5 Open End; weft count, 15 Open End; weight, 204 g.m⁻².

Alum (KAl(SO₄)₂·12H₂O, Fluka), ferrous sulphate hydrate (FeSO₄·7H₂O, Riedel-de-Haen), and stannous chloride (SnCl₂, Aldrich), Tannic acid were laboratory reagents grade and were used without further purification.

Commercial Mimosa extract was obtained from Silvateam (Italy). Two cationising agents Croscolor DRT and Croscolor CF were provided from Eurodye-CTC (Belgium). The cationic exchange capacity of these cationising agents was determined by firstly a mineralization in concentrated nitric acid at 90 °C during 30 minutes under reflux then titration of the chloride ions formed in solution using the Mohr method (Rodier, 1997a). The cationic exchange capacity of Croscolor DRT and Croscolor CF were 84.96 and 73.59 mEq.g⁻¹ of Cl⁻, respectively.

Olive mill wastewater (OMW) used

The OMW used in this study was obtained from an arranged evaporating pond, which is located in the region of Monastir (Menzel Hareb). A sufficient amount of OMW was taken to enable performing a lot of tests for each experiment.

2.2. Preparation of dyeing bath from OMW

The solid waste was eliminated from fresh OMW by filtration. Then, the extraction of residual oil was performed using hexane as solvent. This operation was repeated many times in order to obtain an aqueous fraction of OMW with good quality. The collected liquor was used as dyeing baths for the colouration of woolen fabrics. The pH measured at ambient temperature was acidic about generally 5.

2.3. Gas chromatography–mass spectrometry (GC–MS) analysis of OMW aqueous extract

In order to characterize phenolic compounds in the used OMW, the product was isolated from the solution by first acidifying it to a pH < 2 with sulphuric acid (1 N), 4 mL of the acidified solution was extracted with ethyl acetate for three times (8 mL). Then, the solution was subjected to a mild stream of nitrogen to be concentrated. The sample was dissolved in 200 µL ethyl acetate and converted into trimethylsilyl ethers with a silylation mixture made up of 200 µL N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 100 µL of pyridine for 2 h at room temperature. The solvent was removed under a stream of nitrogen and trimethylsilyl derivatives were analysed by gas chromatography coupled with mass spectrometry (GC–MS). The analysis was run on a Hewlett-Packard GC-MS system (GC: 5890 Series II; MSD 5972). The fused-silica HP-5 MS capillary column (30 m × 0.25 mm i.d., film thickness of 0.25 µm) was directly coupled to the MS. The carrier gas was helium, with a flow rate of 1.7 mL min⁻¹; The GC oven temperature was programmed as follows: 100 °C hold for 1 min, raised at 4 °C/min to 260 °C (held for 10 min). Mass spectra were obtained in electron impact ionization at 70 eV. The components of the OMW aqueous extract were identified by comparison their mass spectra with those of a computer library (Wiley 275L mass spectral library).

2.4. Fabric treatment before dyeing

The cotton fabrics were treated with a solution containing 4 % (w/w with respect to the fabric) of Tannic acid, Mimosa powder extract, Croscolor DRT or Croscolor CF at 50 °C for 60 min, keeping the material to liquor ratio of 40:1. Then, they were squeezed off to a liquor pick-up of 90% and dried.

2.5. Dyeing without a mordant

The fabrics were dyed at a liquor ratio of 40:1. The temperature was raised to 100 °C over 30 min and maintained at this level for 60 min. The dyeing was carried out in laboratory dyeing machine (Ahiba Datacolor International, USA). The dyed fabrics were then rinsed with water, followed by soaping with 2 g.L⁻¹ of a non-ionic soap (Cotoblanc RS, Bezema) at 60 °C. Finally, the fabric samples were washed thoroughly with cold water, squeezed and dried.

Dyeing with mordants

The three different methods of dyeing employed were pre-mordanting, meta-mordanting and post-mordanting. Several mordants such as aluminium sulphate hydrate (Alum), ferrous sulphate and stannous chloride were used with a concentration of 3% (w/w with respect to the fabric).

In the pre-mordanting method, the fabrics were first soaked in an aqueous solution of mordant for 45 min at 30 °C. Then, the mordanted fabrics were dyed by the above method.

For the meta-mordanting method, the fabrics were immersed in the OMW dyebath containing a mordant. The temperature was raised to 100 °C over 30 min and held for 60 min. The fabrics were rinsed, soaped with non-ionic soap (Cotoblanc RS, Bezema) at 60 °C, washed with water, squeezed and dried.

In the post-mordanting method, dyeing was performed in the absence of a mordant, followed by mordanting in a separate bath containing a mordant at 30 °C for 45 min. Further processing was the same as described in the meta-mordanting method. Each dyeing experiment with or without mordant was performed in triplicate.

Dyeing quality evaluation

The reflectance values and the corresponding CIElab L*, a*, b*, C*, h* and colour yield (K/S) values were measured by SpectroFlash SF300 spectrophotometer with dataMaster 2.3 (Datacolor International, USA) using D₆₅ and 10° standard observer. L*, a*, b*, C* and h* represent lightness, redness-greenness of colour, yellowness-blueness of colour, saturation of colour, and hue value, respectively. The colour yield (K/S) value was calculated from the reflectance values at 410 nm (the wavelength of maximum absorbance) using the Kubelka-Munk equation (Kubelka, 1948; 1954) as follow:

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

Where R is the decimal fraction of the reflectance of dyed fabric, R₀ is the decimal fraction of the reflectance of undyed fabric, K is the absorption coefficient and S is the scattering coefficient. For the evaluation of (K/S), the higher the value is, the greater the colour yield is.

In case of dyeing with mordants, the shades may vary. So, the dyeing performances of the dyed samples were appreciated by measuring the Sum(K/S) which is calculated as follow:

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

All experiments were performed in triplicate and the results were given in terms of mean value.

2.6. Fastness testing

The dyed samples were tested according to French standard methods. The specific tests were for colour fastness to washing NF G 07-200, colour fastness to rubbing NF G 07-016, colour fastness to light NF G 07-067 and colour fastness to perspiration NF G 07-013-4.

2.7. Residual dyebaths analyses

Determination of total polyphenols concentration in dyebaths before and after dyeing was carried out with a CECIL 2021 Instruments UV/Vis spectrophotometer at 765 nm using the Folin-Ciocalteu reagent and gallic acid as standard (Singleton and Rossi, 1965). Total polyphenols removal $TP_{rem}(\%)$ was determined using the following equation:

$$TP_{rem}(\%) = \frac{C_{in} - C_{fi}}{C_{in}} \times 100$$

Where C_{in} and C_{fi} are the total polyphenols concentrations in dyebath before and after dyeing, respectively.

Analysis of Chemical Oxygen Demand COD in dyebaths before and after dyeing was determined by the procedure described in (Harrelkas et al., 2008). $COD_{rem}(\%)$ was determined using the following equation:

$$COD_{rem}(\%) = \frac{COD_{in} - COD_{fi}}{COD_{in}} \times 100$$

Where COD_{in} and COD_{fi} are the Chemical Oxygen Demand of dyebath before and after dyeing, respectively.

The Biological Oxygen Demand BOD_5 was analysed according to (Rodier, 1997b).

$BOD_{5rem}(\%)$ was determined using the following equation:

$$BOD_{5rem}(\%) = \frac{(BOD_5)_{in} - (BOD_5)_{fi}}{(BOD_5)_{in}} \times 100$$

Where $(BOD_5)_{in}$ and $(BOD_5)_{fi}$ are Biological Oxygen Demand of dyebath before and after dyeing, respectively.

For the determination of total polyphenols concentration, Chemical Oxygen Demand COD and Biological Oxygen Demand BOD_5 , in dyebaths, all experiments were performed in triplicate and the results were given in terms of mean value.

3. RESULTS AND DISCUSSION

3.1. Characterization of the used OMW

The aqueous OMW fraction was analysed by means of GC–MS and representative chromatogram is shown in Figure 3. The identification of the different peaks of the gas chromatogram was achieved from the mass spectra of their trimethylsilylated derivatives by comparison to reference compounds in Wiley 275L mass spectral library. The abbreviated mass spectra of main organic compounds identified in the ethyl acetate extract from the used OMW in this study are reported in Table 1.

From Figure 3 and Table 1, it can be observed that several phenolic compounds such as homovanillic alcohol, hydroxycinnamic acid, hydroxytyrosol, syringic acid, protocatechuic acid, caffeic acid and ferulic acid which are generally known present in the OMW composition are not recorded in the present GC–MS chromatogram. This may be due to their rapid oxidation with atmosphere's oxygen and light in the evaporating ponds (Azabou et al., 2010).

However, the chromatogram of Figure 3 reveals the presence of Tyrosol which is the common phenolic compound of OMW. Other phenolic compounds such as pyrocatechol, 3-propylphenol, 2-propylphenol,

Tyrosol acetate were also detected. They are probably by-products of oxidation of the phenolic compounds mentioned previously.

Table 1: Abbreviated mass spectra of the main compounds recovered from OMW by ethyl acetate extraction

| TMS derivatives of | Retention time (min) | Pick area (%) |
|--|----------------------|---------------|
| Hexanoic acid | 7.98 | 1.34 |
| Cyclohexanecarboxylic acid | 9.55 | 0.17 |
| O-(trimethylsilyl)- pyrocatecol | 10.09 | 1.67 |
| Pyrocatechol | 10.30 | 1.23 |
| 2,4-Hexadienedioic acid, dimethyl ester, (Z,Z) | 13.14 | 1.64 |
| 2,4-Hexadienedioic acid, dimethyl ester, (E,E) | 13.43 | 4.29 |
| 2-hydroxy-benzeneethanol | 13.87 | 0.99 |
| 3-propylphenol | 14.15 | 2.65 |
| 3-hydroxy-benzeneethanol (Tyrosol) | 14.25 | 0.40 |
| 4-hydroxy-benzene ethanol, | 14.60 | 8.83 |
| 2-propylphenol | 15.08 | 16.83 |
| Tyrosol acetate | 16.20 | 1.81 |
| 3-Butenoic acid, 2-methyl-, methyl ester | 16.68 | 0.86 |
| Salicylic acid, ethyl ester | 17.23 | 3.60 |
| Mandelic acid, methyl ester | 17.47 | 1.13 |
| 4-Hexenoic acid, 6-hydroxy-4-methyl-, methyl ester | 18.26 | 0.43 |
| Diphenylacetaldehyde | 19.72 | 1.29 |
| Oleic acid | 20.76 | 0.14 |
| 4-vinylphenol | 23.01 | 0.09 |
| 4-methyl-benzaldehyde | 26.20 | 1.14 |

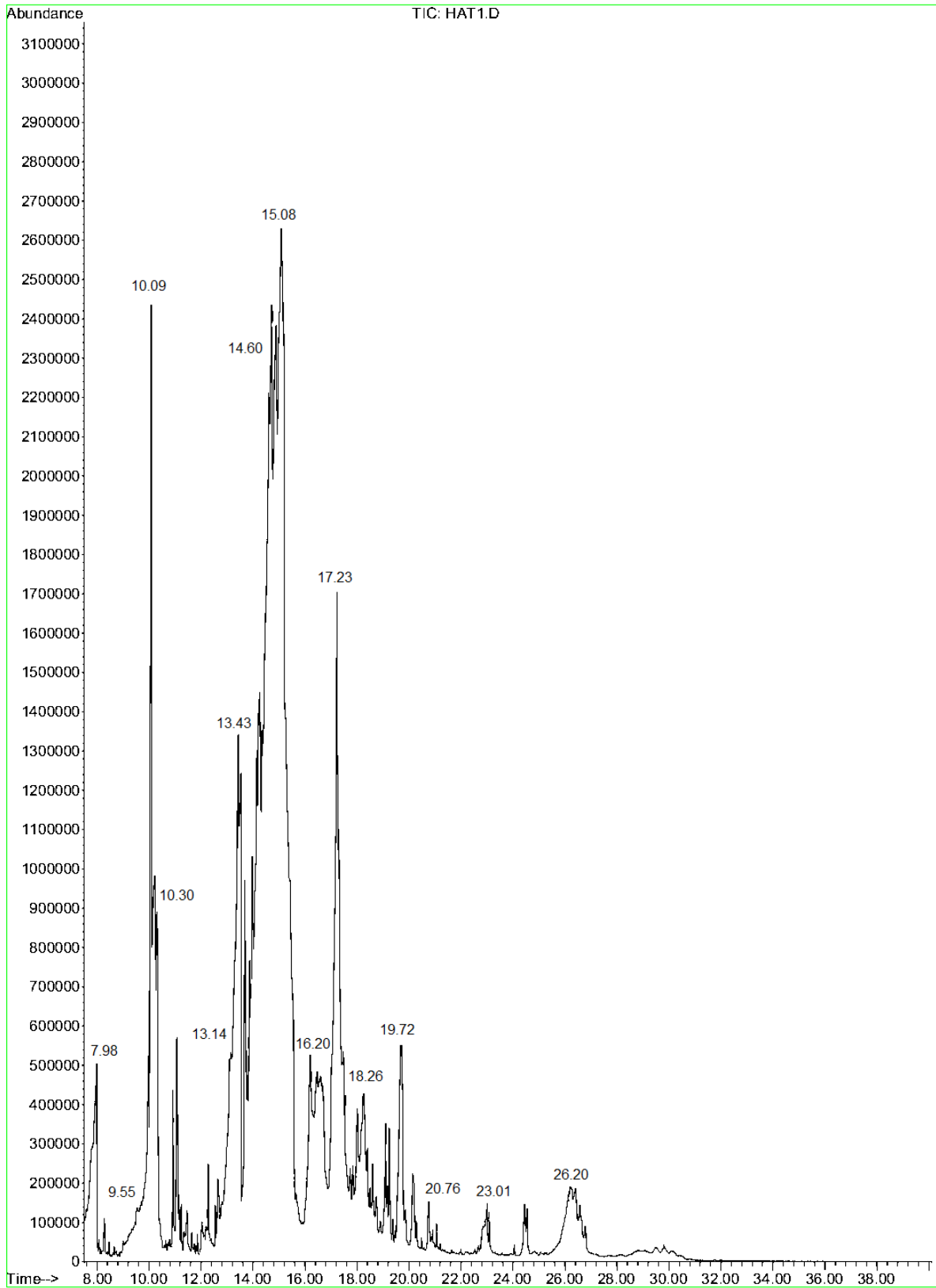


Figure 3: GC-MS chromatogram of ethyl acetate-extractable products obtained from the used olive mill wastewater (OMW)

3.2. Effect of the nature of modifying agent

The dyeing of unmodified and several modified cottons were studied in order to evaluate their affinity to the colouring substances of the aqueous OMW fraction. The evaluation of affinity was appreciated by measuring the colour yield (K/S) of the dyed samples. The used modifying agents were: Tannic acid and Mimosa extract as two polyphenols compounds different, Croscolor DRT and Croscolor CF as two different commercial cationising agents. The results of this study are shown in Figure 4. This figure clearly indicates that modifying of cotton enhanced its dyeability by OMW dyes. Indeed, the unmodified cotton had a low affinity to the colouring substances of OMW aqueous extract (K/S = 3.3). However, when cotton was treated by one of the modifying agents cited above, its affinity raised especially in the case of Croscolor DRT and Tannic acid (the colour yields were equal to 12.18 and 8.32, respectively.). For Croscolor DRT and Croscolor CF which are an ammonium quaternary compounds, their affinity to the colouring phenolic compounds of OMW can be explained by the important attraction between both their quaternary ammonium groups present in cationised cottons and these OMW phenolic compounds of which the molecular structures presented an important electronic density due to their highly conjugated system. However, the presence of a great number of quaternary ammonium groups in Croscolor DRT structure according to Croscolor CF may contribute to attain a dyeing yield which is superior to that obtained with Croscolor CF.

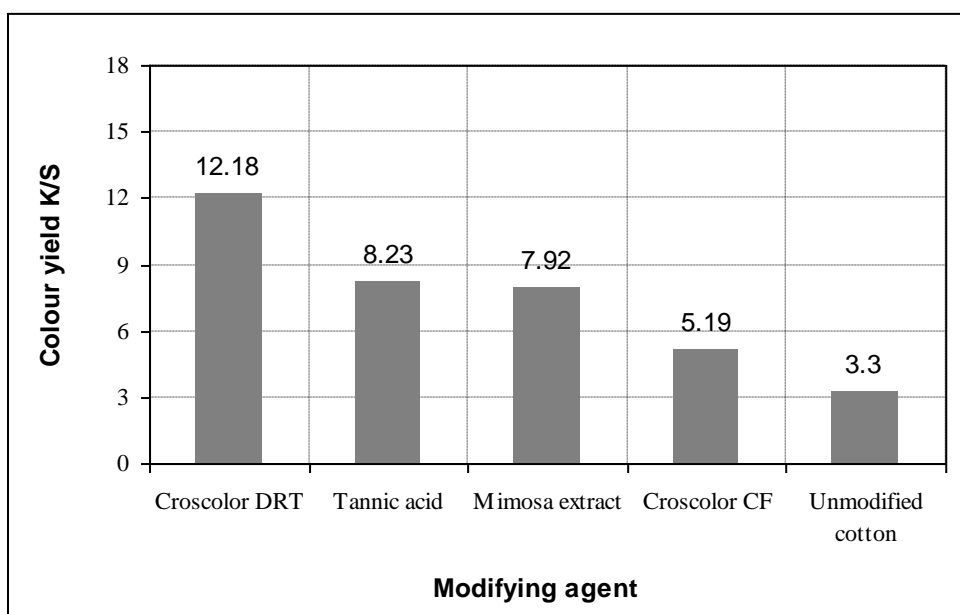


Figure 4: Effect of the nature of modifying agent on the colour yield of dyed cotton fabrics

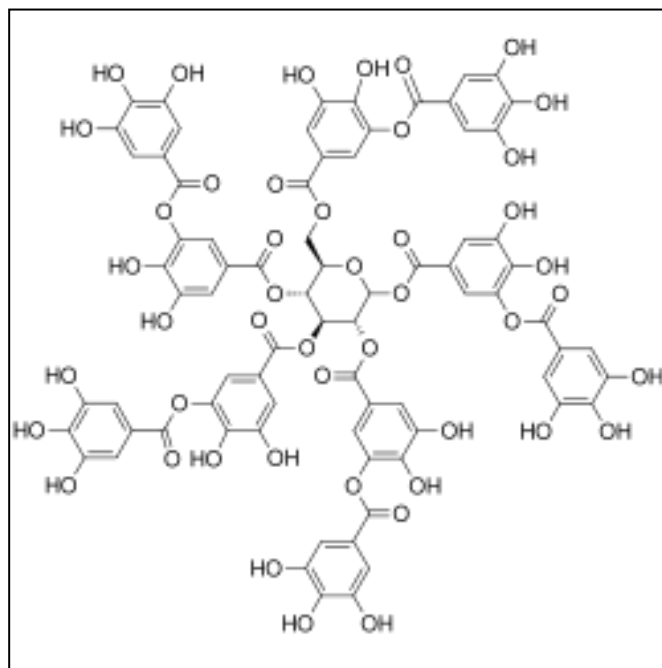


Figure 5: Tannic acid

On the other hand, it was reported that treating cotton with Tannic acid (Figure 5) provides carboxylic acid (-COOH) groups on the fibres (Trotman, 1984; Broadbent, 2001). The high affinity of modified cotton with Tannic acid to the colouring phenolic compounds of OMW can be attributed to the important interaction between the carboxyl groups present in this modified cotton and hydroxyl groups of these OMW phenolic compounds. Whereas, in the case of Mimosa extract, it was reported that this natural substance contains a mixture of condensed tannins which has a polymeric structure containing on the average four flavonoid units, typified by Figure 6 (Martinez, 2002). The percentage of flavonoid units in mimosa tannin is approximately: resorcinol(A)-pyrogallol(B) 56%, resorcinol(A)-pyrocatechol(B) 24%, phlorogucinol(A)-pyrogallol(B) and phlorogucinol(A)-pyrocatechol(B) 20% (Martinez, 2002). It was found that the affinity of cotton treated with mimosa extract to the colouring phenolic compounds of OMW is interesting ($K/S = 7.92$) but remains slightly lower than that of cotton treated with Tannic acid. According to (Hemingway, 1989; Martinez, 2002), B-rings of mimosa tannin (see Figure 6) provide excellent sites for complexation with metals and biopolymers. Their high interaction with the colouring phenolic compounds of OMW may explain probably the good affinity of these colouring substances to the cotton modified with mimosa.

According to these results, Croscolor DRT and Tannic acid were investigated in all next experiments.

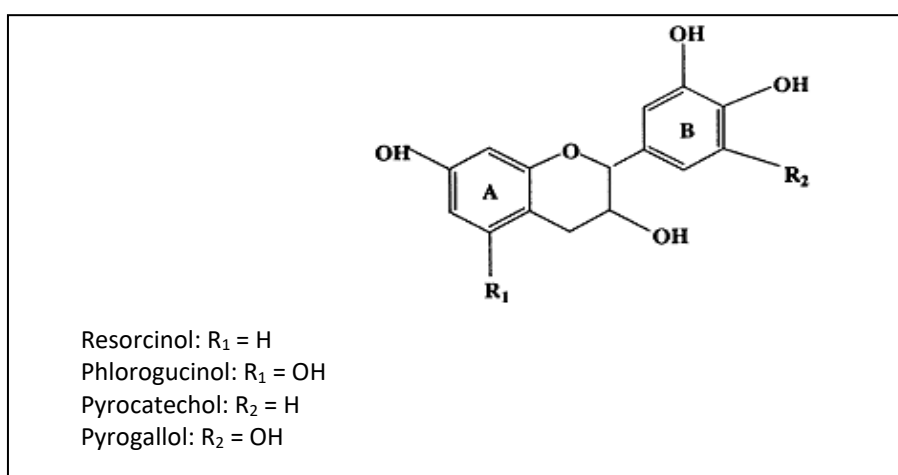
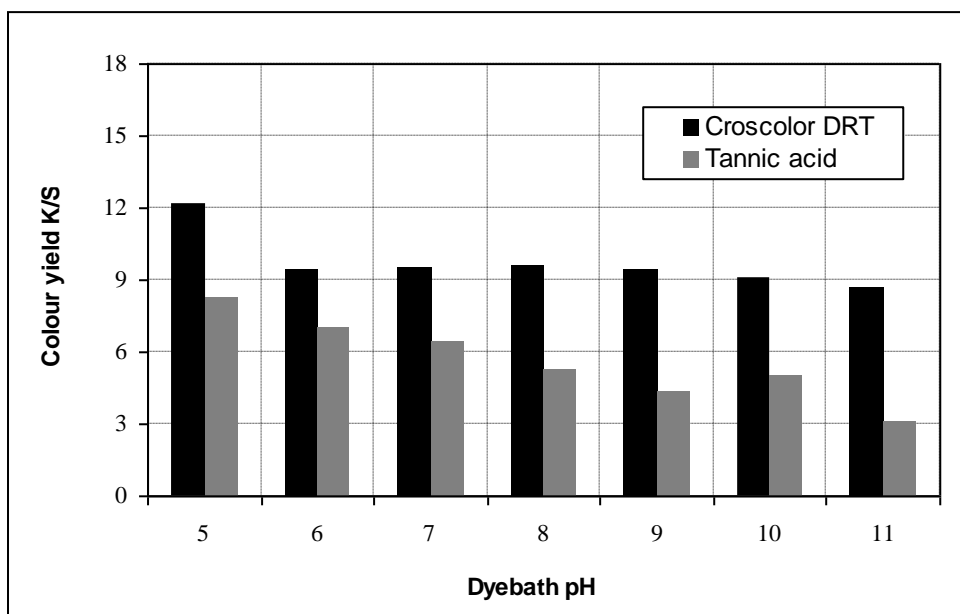


Figure 6: Structure of the flavonoid unit in mimosa

3.3. Effect of dyebath pH

The pH of the dyeing bath was varied from 5 (the initial pH of OMW aqueous extract) to 11. The dyebath pH was adjusted by the addition of sodium hydroxide. The effect of the variation of dyebath pH on the evolution of the colour yield (K/S) for modified cottons with both Croscolor DRT and Tannic acid are reported in Figure 7.



Dyeing conditions: Liquor ratio of 40:1 ; Croscolor DRT amount:4%; Tannic acid: 4%,
Dyebath temperature: 100°C; Dyeing time: 90 min.

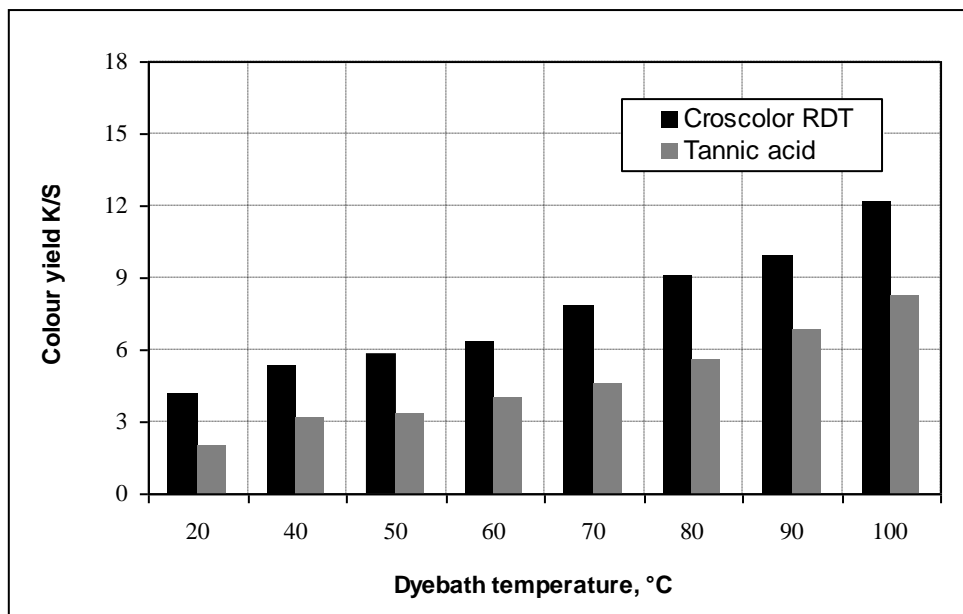
Figure 7: Effect of the dyebath pH on the colour yield of dyed cotton fabrics

This figure reveals that for cationised cotton, when sodium hydroxide was added to reach pH 6 the colour yield (K/S) value decreased slightly, then it remained quite stable with increasing of pH of dyeing bath up to 6. This small decrease of colour yield (K/S) could be attributed to the non stability of some colouring polyphenol spices when sodium hydroxide was added.

In the case of the cotton treated with Tannic acid, it can be seen that when the pH of dyebath increased, the colour yield exhibited a behaviour which was different to that of the cotton treated with Croscolor DRT. From Figure 7, it can be observed that when the pH of the dyeing bath rose, the colour yield (K/S) decreased progressively. This fall can be explained by the repulsion between the hydroxylate anions present in cotton modified with Tannic acid and those of the colouring phenolic substances of OMW. Indeed, when the pH of the dyeing bath increased, both the hydroxyl groups (-OH) of this modified cotton and the hydroxyl groups (-OH) of the OMW polyphenol were ionized to the hydroxylate groups and consequently a repulsion phenomena may occur. It can be also observed from Figure 7 that for all the studied pH of the dyeing bath, Croscolor DRT showed a high colour yield than Tannic acid. According to these results, the pH of dyebath was fixed at around 5 (the initial pH of the OMW aqueous fraction) for all next experiments because it gave the best colour yields.

3.4. Effect of dyebath temperature

The effect of dyebath temperature on the dyeability of the two modified cottons with the OMW aqueous extract was studied at temperatures from 40 to 100 °C. This quality was appreciated by measuring the colour yield (K/S). The results of this study are shown in Figure 8. It was found that for both Croscolor DRT and Tannic acid, the (K/S) values increased with increasing of the dyeing temperature up to 40°C. The result is consistent with increased fibre swelling with higher temperature. This generally leads to a higher dye uptake and an enhancement of dye diffusion (Ahmed, 2005; Kamel et al., 2005).

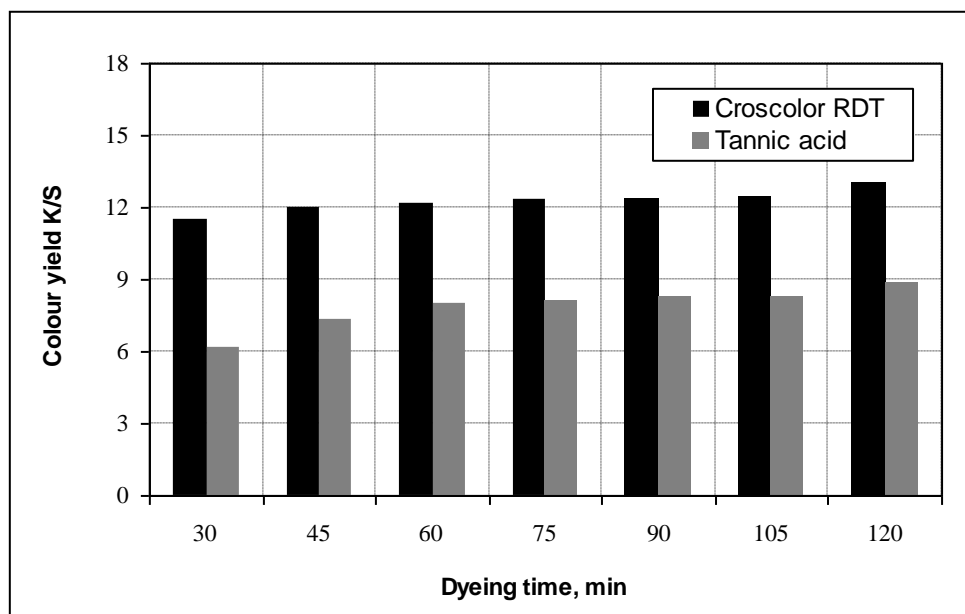


Dyeing conditions: Liquor ratio of 40:1 ; Croscolor RDT amount:4%; Tannic acid: 4%,
Dyebath pH: 5; Dyeing time: 90 min.

Figure 8: Effect of the dyebath temperature on the colour yield of dyed cotton fabrics

3.5. Effect of dyeing time

The effect of dyeing time on the depth of shade (K/S) of the dyed fabrics is shown in Figure 9. From this figure, it can be observed that for the two modifying agents Croscolor RDT and Tannic acid, the (K/S) values increased with increasing the dyeing time up to 60 min. A plateau was attained after 60 min.



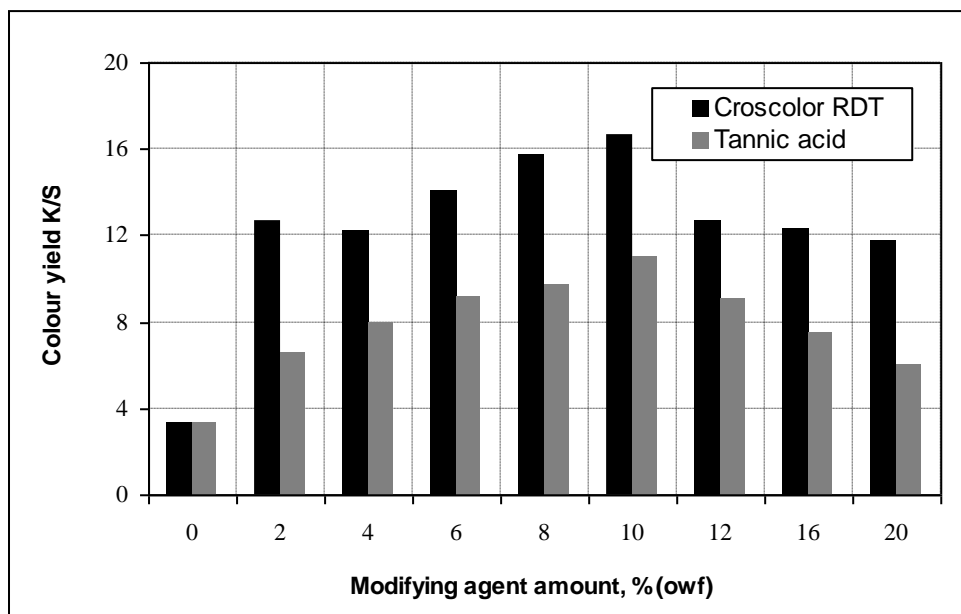
Dyeing conditions: Liquor ratio of 40:1 ; Croscolor RDT amount:4%; Tannic acid: 4%,
Dyebath pH: 5; Dyebath temperature: 100°C.

Figure 9: Effect of the dyeing time on the colour yield of dyed cotton fabrics

3.6. Effect of modifying agent amount

The amount of Croscolor RDT and Tannic acid were varied from 0 to 20% (w/w with respect to the fabric) and the evolution of colour yield (K/S) was investigated. The experimental results are shown in Figure 10. In this figure, it appears that the obtained curves representing the behaviour of the colour yield with the

amount of modifying agent have the same shape for both Croscolor DRT and Tannic acid. In this figure, it can be seen also that each curve is constituted essentially with two parts. The first is an increasing part going from 0 to 10% of the amount of modifying agent. In this part, it can be noted a rapid increasing of the colour yield which attains 16.7 and 11.02 for Croscolor DRT and Tannic acid, respectively at an amount of 10%. This increase of colour yield can be explained by the increase of the modified cottons sites of OMW dye attraction. The second part of the curve begins at 10% of the modifying agent amount. This part shows a rapid decreasing of the colour yield. This fall can be attributed to desorption phenomena.



Dyeing conditions: Liquor ratio of 40:1 ; Dyebath pH: 5; Dyebath temperature: 100°C;
Dyeing time: 90 min.

Figure 10: Effect of the modifying agent amount on the colour yield of dyed cotton fabrics

3.7. Environmental performances of dyeing wastewater

The effect of dyeing of modified cotton with Tannic acid and cationised cotton with Croscolor DRT were investigated in environmental terms. The quality of the corresponding residual dyebaths wastewater was evaluated by measuring the total polyphenols concentration, the Chemical Oxygen Demand COD and the Biological Oxygen Demand BOD₅ in dyebaths before and after dyeing. The obtained results are reported in Table 2. The polyphenols absorption capacity, the polyphenols removal, the COD removal and the BOD₅ removal were also determined after dyeing cotton treated with 10% Tannic acid and cotton cationised with 10% Croscolor DRT with OMW extract. These results are given in Table 3.

Table 2 reveals that the OMW aqueous extract used as dyebath contained a high load of organic matter. This was confirmed by the high values of COD (equal to 75000 mg. L⁻¹) and BOD₅ (equal to 6500 mg. L⁻¹) obtained. Besides, it was found that the initial dyebath is characterized also by high content of polyphenols (4.754 g. L⁻¹). These data show clearly that the direct disposal of this effluent may pollute both land and aquatic environments.

Table 2: Total polyphenols, COD and BOD₅ of the dyebaths before and after dyeing for cotton treated with 10% Tannic acid and cotton cationised with 10% Croscolor DRT

| | Total polyphenols (g.L ⁻¹) | COD (mg.L ⁻¹) | BOD ₅ (mg.L ⁻¹) |
|---|---|---------------------------|--|
| Before dyeing | 4.754 | 75000 | 6500 |
| After dyeing of cotton treated with 10% Croscolor DRT | 3.200 | 31200 | 2400 |
| After dyeing of cotton treated with 10% Tannic acid | 3.774 | 22500 | 3000 |

Table 3: Polyphenols absorption capacity, polyphenols removal, COD removal, BOD₅ removal
Values obtained after dyeing of cotton treated with 10% Tannic acid and cotton cationised with 10% Croscolor DRT by OMW aqueous extract

| | Polyphenols absorption capacity (mg.g ⁻¹) | Polyphenols removal (%) | COD removal (%) | BOD ₅ removal (%) |
|---------------------------------------|---|----------------------------|--------------------|---------------------------------|
| Cotton treated with 10% Croscolor DRT | 62.16 | 32.68 | 58.40 | 63.07 |
| Cotton treated with 10% Tannic acid | 39.20 | 20.61 | 70 | 53.84 |

From Table 2 and 3, it can be seen that the elaborated dyeing process enables to decrease significantly the polyphenols concentration in the dyebath. The polyphenols removal obtained in the case of modified cotton with Tannic acid and cationised cotton with Croscolor DRT are 20.61 and 32.68%, respectively. These results show firstly that polyphenols are the major colouring substances absorbed by modified cotton fibres. Then, they confirm previous results that these colouring substances possessed more affinity to cationised cotton than that of modified cotton with Tannic acid. The polyphenols absorption capacity of cationised cotton was 62.16 mg.g⁻¹ whereas the polyphenols absorption capacity of modified cotton with Tannic acid was 39.20 mg.g⁻¹.

On the other hand, the developed dyeing process enables also to decrease considerably the pollutant load of the OMW aqueous extract (the initial dyebath). From Table 2 and 3, it can be observed that the values of the COD removal and the BOD₅ removal were very important for both cationised cotton with Croscolor DRT and modified cotton with Tannic acid. The values of COD removal obtained for the two textile materials were 58.40 and 70%, respectively. The values of their BOD₅ removal were 63.07 and 53.84%, respectively.

From these values, it appears that cationised cotton with Croscolor DRT reduced more the Biological oxygen demand BOD₅ of dyeing bath than cotton modified with Tannic acid. Whereas, cotton modified with Tannic acid reduced more the Chemical oxygen demand COD of dyebath. This means that compounds absorbed by cationised cotton were more oxidable by biological process than by chemical process. This is contrary to the case of modified cotton by Tannic acid.

According to these results, it can be deduced that the developed process of dyeing cotton by the aqueous extract of OMW using Croscolor DRT or Tannic acid is an ecological process because it contributes to decrease remarkably the pollution generated by this effluent. After dyeing, the residual dyebaths can be obviously used again to colour modified cotton fibres and the polyphenols load can be consequently more decreased.

3.8. Effect of mordanting on dyeing properties

The three mordanting methods (pre-mordanting, meta-mordanting and post-mordanting) were used and several mordants including aluminum sulphate hydrate (Alum), ferrous sulphate and stannous chloride were investigated for both cotton treated with Tannic acid and cotton cationised with Croscolor DRT. Varied hues of brown colours were obtained using mordanting processes. The colorimetric data of cationised cotton with Croscolor RDT and modified cotton with Tannic acid are shown in Table 4 and 5, respectively. Due to the great variation of hue h^* of the dyed samples, the dyeing performances were appreciated by measuring the Sum(K/S) between 400 and 700 nm. Higher Sum(K/S) values indicate higher dyeing yield and deeper colours. It was found that for the pre-mordanting method, the Sum(K/S) value of the mordanted modified cottons increased in the order of dyeing using:

$$\text{SnCl}_2 < \text{Alum} < \text{None} < \text{FeSO}_4$$

From these results, it can be observed that sulphate ferrous gave the highest colour yield. However, alum and stannous chloride gave the lowest yields which are inferior even to that of the unmordanted modified cotton.

On the other hand, using the meta-mordanting method, the Sum(K/S) value of the mordanted cationised cotton with Croscolor DRT increased in the order of dyeing using:

$$\text{SnCl}_2 < \text{Alum} < \text{FeSO}_4 < \text{None}$$

and the Sum(K/S) value of the mordanted modified cotton with Tannic acid increased in the order of dyeing using:

$$\text{Alum} < \text{SnCl}_2 < \text{FeSO}_4 < \text{None}$$

These results clearly show that for the two kinds of modified cotton, the meta-mordanting method decreased the colour yield of dyeing and especially when using alum and stannous chloride. This decrease can be explained by the decrease in the effective dye concentration in the dyebath. This is the result of some of the dye substances which are lost because of the formation of an insoluble complex in the dyebath itself when mordants were added.

In the case of the post-mordanting method, it was found that the Sum(K/S) value of the mordanted cationised cotton with Croscolor DRT increased in the order of dyeing using:

$$\text{None} < \text{SnCl}_2 < \text{Alum} < \text{FeSO}_4$$

and the Sum(K/S) value of the mordanted modified cotton with Tannic acid increased in the order of dyeing using:

$$\text{SnCl}_2 < \text{Alum} < \text{None} < \text{FeSO}_4$$

Table 4: The dyeing results, colour yield (K/S), Sum (K/S) and the colorimetric data (L^* , a^* , b^* , C^* and h^*) for the dyed samples with and without metallic salts in the case of cotton fabrics cationised with 10% Croscolor DRT

| Method | Mordant | Shade | Sum (K/S) | L^* | a^* | b^* | C^* | h^* |
|--------------------|-------------------|-------------|-----------|-------|-------|-------|-------|-------|
| Without mordanting | - | Brown | 214.45 | 30.70 | 4.16 | 7.86 | 8.89 | 62.11 |
| Pre-mordanting | Alum | Brown | 165.76 | 34.34 | 4.53 | 8.65 | 9.77 | 62.37 |
| | Ferrous sulphate | Grey-Brown | 226.89 | 29.84 | 3.56 | 7.22 | 8.05 | 63.74 |
| | Stannous chloride | Brown | 137.03 | 37.57 | 5.28 | 10.92 | 12.13 | 64.18 |
| Meta-mordanting | Alum | Light Brown | 125.25 | 38.31 | 4.69 | 8.78 | 9.95 | 61.89 |
| | Ferrous sulphate | Grey-Brown | 190.29 | 32.15 | 3.25 | 6.95 | 7.67 | 64.97 |

| | | | | | | | | |
|-----------------|-------------------|-----------------|--------|-------|------|-------|-------|-------|
| | Stannous chloride | Hazelnut | 109.12 | 42.27 | 8.85 | 15.98 | 18.27 | 61.01 |
| | Alum | Dark Brown | 294.05 | 26.52 | 4.18 | 7.50 | 8.59 | 60.85 |
| Post-mordanting | Ferrous sulphate | Dark Grey-Brown | 328.38 | 25.09 | 3.24 | 6.73 | 7.47 | 64.29 |
| | Stannous chloride | Brown | 262.55 | 28.18 | 4.66 | 8.46 | 9.66 | 61.14 |

Table 5: The dyeing results, colour yield (K/S), Sum (K/S) and the colorimetric data (L*, a*, b*, C* and h*) for the dyed samples with and without metallic salts in the case of cotton fabrics treated with 10% Tannic acid

| Method | Mordant | Shade | Sum (K/S) | L* | a* | b* | C* | h* |
|--------------------|-------------------|------------------|-----------|-------|------|-------|-------|-------|
| Without mordanting | - | Brown | 199.20 | 31.43 | 4.84 | 7.31 | 8.76 | 56.48 |
| | Alum | Brown | 179.49 | 33.30 | 5.42 | 9.07 | 10.57 | 59.13 |
| Pre-mordanting | Ferrous sulphate | Dark Grey-Brown | 303.19 | 25.63 | 3.18 | 5.12 | 6.03 | 58.19 |
| | Stannous chloride | Dark Hazelnut | 159.92 | 36.12 | 7.83 | 13.27 | 15.41 | 59.45 |
| | Alum | Light Brown | 84.66 | 44.08 | 5.21 | 9.24 | 10.61 | 60.60 |
| Meta-mordanting | Ferrous sulphate | Light Grey-Brown | 189.09 | 31.62 | 3.36 | 4.58 | 5.67 | 53.73 |
| | Stannous chloride | Light Hazelnut | 86.98 | 45.16 | 7.91 | 14.58 | 16.58 | 61.52 |
| | Alum | Dark Brown | 196.29 | 32.02 | 4.91 | 8.66 | 9.95 | 60.47 |
| Post-mordanting | Ferrous sulphate | Grey-Brown | 252.44 | 28.29 | 3.24 | 6.27 | 7.06 | 62.67 |
| | Stannous chloride | Light Brown | 157.12 | 35.23 | 5.09 | 9.30 | 10.60 | 61.33 |

From Table 4 and 5, it can be concluded that the best values are obtained with ferrous sulphate as mordant. Thus, in all cases of mordanting processes, iron provided dark shades. This can be attributed to the ability of iron to form coordination complexes with the olive dyes. As the coordination numbers of iron are 6, some coordination sites remained unoccupied when they interacted with the fibre. Functional groups such as amino or carboxylic acid groups on the modified fibre can occupy these sites. Thus, these metals can form a ternary complex on one site with the fibre and on the other site with the dye substances. Such a strong coordination tendency can enhance the interaction between the fibre and the dye compounds, resulting in high dye uptake.

In addition, it can be noted that contrary to iron, alum and stannous chloride increased generally the saturation C*, a* and b* parameters of the dyed samples. Thus, the shades became more red, yellow and bright. This was observed nearly for all mordanting processes.

3.9. Effect of mordanting on fastness properties of dyed fabrics

For Croscolor DRT and Tannic acid, the rating of fastness (light, washing, rubbing and perspiration fastness) of unmordanted and mordanted fabrics dyed with olive mill wastewater are shown in Table 6 and 7, respectively. It was found that washing, rubbing and perspiration fastness of unmordanted modified cotton and unmordanted cationised cotton were generally good (4 to 5 units on the grey scale whereas 5 is the highest rating). This result can be attributed to the high affinity between OMW dyes and treated cottons. However, the light fastness of unmordanted treated cotton fabrics remained poor (2 units on the standard blue scale whereas 8 is the highest rating). This low performance towards light is well known for many natural dyes (Lee, 2007; Hwang et al., 2008). Table 6 and 7 show also that

mordanting improved slightly washing, rubbing and perspiration fastnesses and considerably light fastness. The best results were obtained especially with iron as mordant (3 to 4 units on the standard blue scale). The post-mordanting presents a more significant improvement than other mordanting processes. It can be noted also that the nature of modifying agent (Tannic acid or Croscolor DRT) has no effect on the fastnesses degree of the dyed samples.

Table 6: Fastness properties of the dyed samples with and without metallic salts in the case of cotton fabrics cationised with 10% Croscolor DRT

| Method | Mordant | Wash NF G 07-200 | Light NF G 07-067 | Rubbing NF G 07-016 | | Perspiration NF G 07-013-4 | |
|--------------------|-------------------|---------------------|----------------------|---------------------|-----|----------------------------|----------|
| | | | | Dry | Wet | Acidic | Alkaline |
| Without mordanting | - | 4-5 | 2 | 4-5 | 3 | 4 | 3-4 |
| Pre-mordanting | Alum | 4-5 | 3 | 4 | 4 | 4 | 4 |
| | Ferrous sulphate | 5 | 3 | 5 | 4 | 3 | 3-4 |
| | Stannous chloride | 4-5 | 3 | 4-5 | 4 | 4 | 3-4 |
| Meta-mordanting | Alum | 4-5 | 3 | 5 | 4 | 4 | 4-5 |
| | Ferrous sulphate | 5 | 3 | 5 | 4 | 3 | 4 |
| | Stannous chloride | 4-5 | 3 | 5 | 4 | 4 | 4-5 |
| Post-mordanting | Alum | 4-5 | 3 | 5 | 4 | 4 | 4 |
| | Ferrous sulphate | 4-5 | 4 | 5 | 4-5 | 3-4 | 4 |
| | Stannous chloride | 4-5 | 2 | 4 | 4 | 4 | 4 |

Table 7: Fastness properties of the dyed samples with and without metallic salts in the case of cotton fabrics treated with 10% Tannic acid

| Method | Mordant | Wash NF G 07-200 | Light NF G 07-067 | Rubbing NF G 07-016 | | Perspiration NF G 07-013-4 | |
|--------------------|-------------------|---------------------|----------------------|---------------------|-----|----------------------------|----------|
| | | | | Dry | Wet | Acidic | Alkaline |
| Without mordanting | - | 4 | 2 | 4-5 | 3 | 4 | 4 |
| Pre-mordanting | Alum | 4 | 3 | 5 | 3-4 | 4 | 4 |
| | Ferrous sulphate | 4-5 | 3 | 5 | 4 | 3-4 | 3-4 |
| | Stannous chloride | 4 | 2 | 5 | 4 | 4 | 4-5 |
| Meta-mordanting | Alum | 4-5 | 3 | 5 | 3-4 | 4 | 4 |
| | Ferrous sulphate | 4-5 | 4 | 5 | 4 | 3 | 4 |
| | Stannous chloride | 4 | 3 | 5 | 4 | 4 | 4-5 |
| Post-mordanting | Alum | 4-5 | 3 | 5 | 4-5 | 4-5 | 4-5 |
| | Ferrous sulphate | 5 | 4 | 5 | 4-5 | 4 | 3-4 |
| | Stannous chloride | 4-5 | 2 | 5 | 4 | 4 | 3-4 |

4. CONCLUSION

This paper describes the feasibility of dyeing of cotton, the most important textile fibre in the world, by natural colorants extracted from olive mill wastewater (OMW). The developed process required the pre-treatment of cotton fibres by cationising agent (Croscolor DRT) or phenolic compound such as Tannic acid.

It was found that cotton cationised with Croscolor DRT gave usually the higher colour yield than cotton modified with Tannic acid. The obtained shades were brown with good fastness properties.

In terms of environmental performances, the developed dyeing process reduced considerably the Chemical Oxygen Demand COD and the Biological Oxygen Demand BOD₅ of the olive mill wastewater as well as its content of polyphenols and contributed consequently to resolve the ecological problem caused by this effluent.

The developed process can achieve an eco-friendly and economically viable dyeing process as the raw material is renewable, available and cheap. So, the cost of production is very low. It can thus be recommended for industrial application.

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