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RESEARCH ARTICLE

WINE WASTE MANAGEMENT: DYEING WOOL FABRIC WITH GRAPE POMACE

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ABSTRACT

Grape pomace, which is winery waste, has been studied and experimented to serve as sources for natural dyes in textile dyeing operations. The water: ethanol mixture of 90:10 (v/v) is used for extraction of anthocyanin at 40ºC from different Tunisian grape varieties. The anthocyanins amount varies from 100 mg to 3200 mg per kilogram of grape pomace variety. The extract has been used for dyeing wool fabrics. This study will tackle exhaustively the following points: the effects of some parameters such as temperature, pH, salt addition and the number of dyeing bath reuse, on wool dyeing with the grape pomace extract. Besides, tannic acid was used to improve dye fastness proprieties.

INTRODUCTION

Recently an important interest in the use of natural dyes in textile coloration has been growing. This is a result of the strict environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes. Natural dyes are more eco-friendly than synthetic dyes and can show better biodegradability. Anthocyanins can be used as natural dyes. In fact they are plant pigments that can be found in blood orange, radish, carrot, grape, strawberry…etc. Grapevine is an important source of these compounds. Anthocyanin can be found in all parts of the plant genotypes (stems, leaves, grape seeds and roots). Grape, grape seeds, grape pomace and vine leaves don't contain one anthocyanin but several (Bechtold, Mahmud, & Mussak, 2007) in different proportions. This profile is very much dependent on the date of harvest (Ezzili & Darne, 1999). These compounds have been studied for possible biological activities. Besides, it has been demonstrated that the bright red and blue are useful for coloring textiles (Aslanov & Gorchev, 1976; Chae & Choung, 2000; Strigl *et al.,* 1995).

Grape anthocyanins may have the range of red / purple (Bechtold & Mussak, 2006; Kim, 2000; Giusti & Wrolstad, 2001). Purple may be interesting but the direct employment of the grape is not desired because the grapes can contain 160-250g sugar / kg. However, the waste of wine industry can be a valuable commodity (Tashiro & Kojiri 1972) as there are between 10 tons and 20000 tons of waste per year, from different Tunisian grape varieties. Grape pomace contains rich anthocyanin of high quality, non-toxic, antioxidant, antibacterial and harmless natural pigments (Kahkônen *et al.,* 2003; Chae & Choung 2000; Mitka & Nowak, 2003). However, the variation of the amount of anthocyanins from one variety to another is a significant problem for reproducibility (Bechtold & Mussak, 2006; Giusti & Wrolstad, 2001). Anthocyanins are polar molecules with hydroxyl, carboxyl, methoxyl and glycolyl groups bound to aromatic rings. They are more soluble in water than in non polar solvents and this characteristic helps extraction and separation processes, as described by Harbone and Grayer (1988). Hydrochloric acid diluted in methanol is generally used to extract anthocyanins. In aqueous extractions, the most used and efficient acids are acetic, citric, tartaric and hydrochloric. Studies on anthocyanin extraction using these solvents are found in literature (Harbone & Grayer, 1988; Francis, 1989; Bridle *et al.,* 1997; Montes *et al.,* 2005). The two objectives of this work were to extract grape pomace anthocyanins from the main Tunisian grape varieties, in a cleaner way, and to exploit the extract in dyeing wool fabrics. Thus, the water-ethanol mixture of 90:10 (v/v) is used for extraction then the extract will be used for wool fabrics dyeing. The effects of some parameters (temperature, pH, salt addition…etc) on wool dyeing with the extract of grape pomace have been studied. Besides, the fastness of dyeing is also checked.

EXPERIMENTAL DETAILS

Preparation of grape pomace samples

Different samples of grapes are separately collected from the Tunisian group of wine and fruit growers. The grape varieties

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studied are listed in Table 1. We have pressed the grapes. The juice is recuperated for other anthocyanin analysis and Pomaces are dryied at 40°C. We have applied the same methodology for all samples cited in this work. For the anthocyanin analysis, we have used the following analytical grade chemicals: KCl, HCl , NaOAc from Sigma Aldrich.

Extraction of plant dye

The extraction is carried out in 100 ml of the mixture (water: ethanol 90:10), using a constant amount of the dye materials. The standard procedure of the mass of dry grape pomace/volume of liquid ratio is set at 1:20, i.e. 1g of dry grape pomace is extracted with 20 ml of the solution. The extraction is performed in approximately 24h, at 40° C. The amount of the extracted coloured substances has been detected by photometry. The absorbance of the dye liquor at 520 nm is measured. Photometry is used to quantify the extractable amount of coloured material as monomeric anthocyanin pigment (cyanidin3-glycoside).

Quantity of anthocyanins in Tunisian grape pomace by the Spectrophotometric method

The amount of extracted anthocyanin is determined with photometry method by using the pH differential assay of Giusti and Wrostad. Absorbance's are measured photometrically in the interval of 350-700 nm using 10mm cuvettes and zeiss CLH 500 UV-Visible diode array spectrophotometer. Absorbances at 520 and 700 nm in buffers at pH 1 and 4.5 are used to calculate the concentration of dyes as cyanidin-3-glycoside (Figure 1) from as it was used in other work (Bechtold, Mahmud, & Mussak, 2007).

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

Monomeric anthocyanin pigment concentration in extract is then calculated according to Eq(2). Anthocyanin pigment (cyanidin-3-glucoside equivalents, mg/L) =

$$\frac{A \times MW \times DF \times 10^3}{\varepsilon \times l} \qquad (2)$$

Where MW is the molecular weight (= 449.2 g/mol for cyanidin-3-glucoside (cyd-3-glu)), DF is the dilution factor, and l is the path length in cm, ε = 18000 is the molar extinction coefficient, in $L.mol^{-1}.cm^{-1}$. For cyd-3-glu (for the extraction with ethanol/water); and 10^3 is a factor for conversion of g to mg. the determined concentration into a dye content (DC) in the plant material multiplication by a factor of 20 (1 g of material extracted into 20 ml of water).

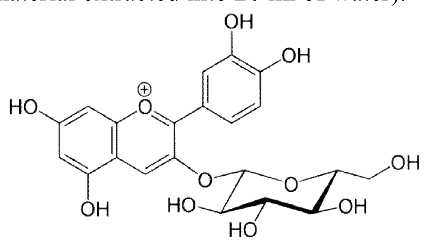

Figure 1: Chemical structure of Cyanidin 3-O-glucoside

Dyeing process

Dyeing is performed by the exhaustion method using a liquor ratio of 1:20 in one dye bath containing different quantities of sodium chloride (0-25 $g.L^{-1}$). The bleached wool fabrics are dyed at different pH (1-10) values, at different temperatures. The effect of the number (1-5) of dye bath reuse is also carried out for both temperatures T= 95ºC and T= 45ºC. The fabrics are treated with a solution containing 5 $g.L^{-1}$ non-ionic detergents and are rinsed three times in cold water. The effect of mordant is studied at both temperatures by following the meta-mordanting method (i.e. dyeing in the presence of mordant), the fabrics are immersed in a dye bath containing a mordant and the dye extract aqueous solutions containing 7.5 $g.L^{-1}$ of tannic acid, and the dye bath is maintained at pH 2. The fabrics are rinsed three times in cold water. The pH values are recorded with Eutech pH meter and adjusted with dilute solutions of sodium hydroxyde and HCl.

Evaluation of dyeing quality

The reflectance and the L, a*, b* values of the dyed samples are measured on a Data Colour UV/Vis spectrophotometer. Relative colour strengths (K/S values) are determined using the Kubelk and Munk equation (Judd & Wysezcki,1975). L corresponding to the brightness (100 = white, 0 = black), a* to the red/green coordinate (positive sign = red, negative sign = green) and *b** to the yellow/blue coordinate (positive sign = yellow, negative sign = blue).

Fastness testing

The dyed samples are evaluated according to NF and ISO standard methods: NF G07- 019-12 for colour fastness to rubbing; ISO 105 C03 for colour fastness to washing and ISO 105-B02 colour fastness to light.

RESULTS AND DISCUSSION

The quantity of anthocyanins in Tunisian grape pomace by the Spectrophotometric method

As the table1 shows, there is an obvious difference in the amount of anthocyanin extracted from the different grape pomace varieties; for example, Mouvèdre contains 100 $mg.kg^{1}$ anthocyanin while Merlot 3200 $mg.kg^{-1}$. On the other hand, the amount of anthocyanin depends on the date of collection. Indeed, on 16/08/2011, for example, Merlot grape pomace contained 1600 mg kg^{-1} of anthocyanin; this quantity increased two times (3200 $mg.kg^{-1}$) on 06/09/2011. Similarly, for Carignan grape pomace, the amount of anthocyanin increased and passed from 530 mg kg^{-1} on 16/08/2011 to the amount of 800 mg kg^{-1} on 06/09/2011, while as far as Mouvedre and Porto grape pomaces are concerned, there was a decrease in the amount of anthocyanin on 16/08/2011 and on 06/09/2011. The date of harvest appears as an important factor influencing anthocyanin content in grape variety. Thus, we cannot have a reproducible anthocyanin quality of grape pomace. For the rest of this study, we will work on the grape pomace carignan variety because it is the most cultivated one in Tunisia.

Dyeing process

To study the effect of temperature, pH, salt addition, number of the dye bath reuse on wool fabrics, the samples are dyed with grape pomace extract under the conditions described in the dyeing procedure.

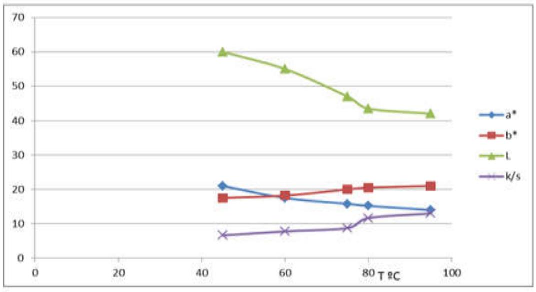

Figure 2: Effect of temperature on a*, b*, L and k/s values of wool fabrics dyed with grape pomace extract

Figure 2 shows the effect of the temperature of dyeing on L*, a*, b* and k/s values. When, the values of temperatures increase, the values of L* decrease while the values of k/s increase. Thus the higher value of L* and lower value of k/s show lighter shades, while lower L* values and higher values of k/s signify deeper shades of dyed wool fabric. Similarly, positive a* and positive b* represent red and yellow; however low value of a* and b* represent respectively green and blue. Therefore, samples dyed at 45ºC have the higher value of a*and low value of b*, while the other ones dyed at 95˚C have the lowest value of a* and the highest value of b*. This result correlates with purple and brown shades obtained which could be explained by the temperature effect on anthocyanin dye chemical structure (Castañeda-Ovando & Lourdes, 2009).

Effect of pH

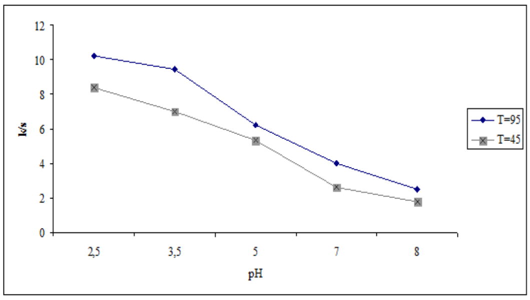

Figure 3: Effect of dye bath pH on the colour strength of wool fabrics dyed with grape pomace at 45ºC and 95ºC.

Figure 3 shows that the pH values of the dye bath have significant effect on the dyeability of wool fabrics with grape pomace at both temperatures. It is clear that at 95˚C the dyeability of the fabrics was improved at pH 1 and 2 values but started to decline abruptly as the pH increases with rather lower dyeability at T= 95˚C. This result can be explained by the correlation between the dye and wool fibre structure. Since the Anthocyanin pigments of grape pomace undergo reversible structural transformations with a change in pH. The colored oxonium form predominates at pH 1.0 and the colorless hemiketal form at pH 4.5 (Castañeda-Ovando & Lourdes, 1998; Trappey & Bawadi, 2005; Shanker & Vankar, 2007). Besides, when wool's pH is inferior to 4.8 (isoelectric wool's pH), it behaves as a weak base and then it has, by consequence, more affinity to ionic dyes. The important amount of anthocyanins in grape pomace has a complex character. When anthocyanins are bound on fibre, further kinds of interactions take place together with ionic forces. Since the dye used containes OH groups, it will interact ionically with the protonated terminal amino groups of wool fibres at acidic pH via ion exchange reaction due to the acidic character of the OH groups. The dye uptake, however, decreases with an increase in pH from neutral to alkaline.

Effect of salt addition

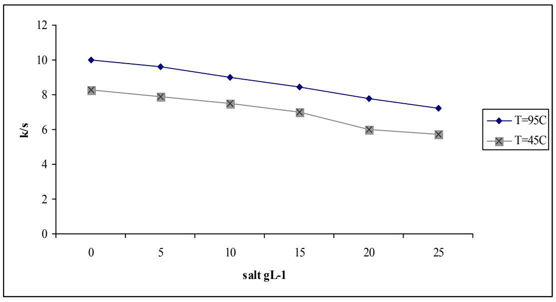

Figure 4: Effect of salt addition to the dye bath on the colour strength of wool fabrics dyed with grape pomace.

It is recognized that in the case of using high affinity acid or reactive dyes in dyeing, salt addition is necessary as it retards the dye migration and thus obtains better quality of dyeing. Figure 4 shows the effect of salt concentration on the colour strength obtained for the dyed fabrics. It is clearly indicated that as the salt concentration increases the colour strength decreases at both temperature 45ºC and 95º C. It is also noticed that at 95˚C, the value of the colour strength was maximum, i.e., dyeing without salt addition is the best condition. This result is similar to those described by other authors (Kamel & El-Shishtawy, 2007; Nagia & EL-Mohamedy, 2007).

Effect of dye bath reuses number

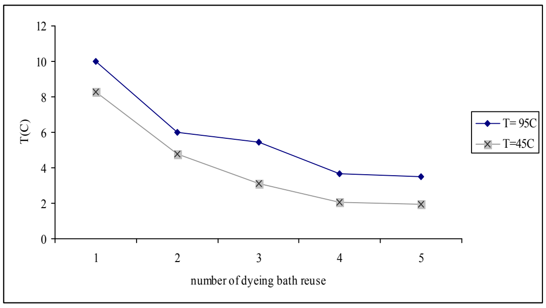

Figure 5: Effect of reuse number of dyeing bath on the colour strength of dyed wool fabrics with grape pomace at 45ºC and 95ºC.

As dyeing has been carried out in concentrated solution of grape pomace dye, it was indispensable to verify the possibility of reusing the dye bath again and see whether the temperature of 95˚C can be rather effective in this case. Figure 5 shows the effect of reuse number on the colour strength obtained. It is clear that dyeing at 95˚C gives more important values of the depths of shade than at 45˚C, and it is remarked that repeating the dye bath reuse always leads to different coloured samples from one batch to another until complete exhaustion of the dye bath. Generally, to evaluate the dyeability of a dyed garment, fastness properties must be done.

Fastness properties

The light, wash, and rubbing fastness values of wool fabrics dyed with and without (tannic acid) are shown at Tables 2a and 2b. The control samples show comparatively good light, rubbing, and wash fastness properties, which were further improved with mordanting. Thus, tannic acid shows the most marked effect on the light fastness of dyed wool samples. This can be attributed to its high molecular weight compounds (1700g mol^{-1}) containing phenolic hydroxyl groups to enable them to form effective cross-links between wool proteins and the anthocyanins. Table 2a shows that there is an increasing of the value of k/s, after the addition of tannic acid. This improvement is possibly thanks to better penetration of the dye molecules in the fibre matrix during meta-mordanting process. As expected the majority of fastness properties of dyed samples are more improved at 95˚C than at 45˚C.

CONCLUSION

The results of this research indicate that the extraction of grape pomace anthocyanin with water: ethanol 90:10 (as cleaner way of extraction) can give an important amount of anthocyanin. The extraction has been carried out at 45 ºC because temperature is an important factor in the degradation of phenolic pigments. Most natural dyes are fragile to heat and are modified and losing their staining properties at elevated temperatures or prolonged heating as shown by many laboratory experiments and industrial practice (Bakker & Bridle, 1992; Markakis, 1982; Jackman & Smith, 1996). Besides, the results show that the concentration of anthocyanins depends on the date of harvest and as it expected it depends on the different varieties of grape pomace. It should be noted, however, that it is impossible to have a reproducible colour from one year to another as evoked by other authors. The technique of "cutting" (mixing anthocyanins at different proportion from different varieties of grape pomace extracts) can make some improvements. Another way to improve colour reproducibility will probably be the use of the pomace extract of only one variety which has been collected on a precise day. Overall and regardless of the colour reproducibility, One-bath dyeing process of wool fabrics with grape pomace extract gives acceptable fastness properties which can be improved with the addition of tannic acid in the same bath. Thus, the use of tannic acid as natural mordant in the same bath of dyeing it is not only a cleaner way as tannic acid is an eco-friendly mordant, but also it is an economic process because it is compared to pre-mordanting or after-treatment methods which are both two bath techniques (Bechtold & Turcanu, 2002).

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