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Environmental Assessment of Osage Orange Extraction and its Dyeing Properties on Protein Fabrics Part I: Standardization of Extraction

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ABSTRACT

Ultrasonic and conventional heating methods were performed to select the best solvent for Osage orange extraction. Distilled water and other co-solvents, such as water-acetone and water-ethanol mixtures were tested at concentrations of 10% v/v. Two grams of Osage orange powder was suspended in 20 cm³ of solvent in a thermostatic and ultrasonic bath. Extraction process was followed by the dyeing of woolen fabric to evaluate data. Ultrasonic assisted extraction at 60°C for 30 min possessed much higher dye absorbance and color strength at lower temperature and time rather than using the conventional heating method. 15% v/v water-acetone co-solvent released 32% of the total dye absorbency and 21% of color strength on the dyed woolen samples, this was followed by water-ethanol co-solvent then water which released 27 and 21% of dye absorbency and 19 and 16% of color strength, respectively. These data are relative to 10, 6 and 4% of dye absorbency and 18, 15 and 11% of color strength with the same co-ordinate solvents in case of using the conventional heating method. Absorption of dye is dependent on solvent polarity. In non-hydrogen-bond donating solvents, solvation of dye molecules probably occurs via dipole-dipole interactions, whereas in hydrogen-bond donating solvents the phenomenon is more hydrogen bonding in nature. Given that both ultrasonic and water acetone co-solvent in extracting Osage orange natural dye, are environmentally and new ecological acceptable for dyeing protein fabrics.

Key words: Environment, ultrasonic, solvent, extraction, osage orang

INTRODUCTION

In the mid 1960s an international awareness of environment, ecology and pollution control has created an upsurge in the interest in natural dyes. Recently, the dye industry is more and more forced to reduce toxic effluents and to stop the production of potentially dangerous dyes or pigments (Glover, 1995).

Osage orange (*Maclura pomifera*) is a tree in the Moraceae family (Cox and Leslie, 1999). The common name is derived from its fruit, which resembles the shape of an orange and from the fact that its hardwood was used by the Osage Indian tribe to make bows. Osage orange is native to Southern Oklahoma and Northern Texas and is planted throughout the United States. Although the fruit is not edible for humans, its extract exhibits antimicrobial and anti-insect activities and the Native Americans have used osage orange for cancer treatment (Mahmoud, 1981). Several

phenolic compounds have been isolated and identified from various parts of this plant, namely, isoflavonoids from the fruit (Wolfrom *et al.*, 1946; Delle Monache *et al.*, 1994), flavonols and xanthenes from the heartwood and stem bark (Wolfrom *et al.*, 1964a; Wolfrom and Bhat, 1965a) and flavanones and xanthenes from the root bark (Wolfrom *et al.*, 1964b; Wolfrom and Bhat, 1965b; Delle Monache *et al.*, 1984).

For technical application of natural dyes, a number of requirements have to be fulfilled. Most problems are derived from technical demands, for example:

- Adaptation of traditional dyeing processes on modern equipment (Deo and Desai, 1999)
- Supply of dye-houses with the required amount of plant material (Bruckner *et al.*, 1997; Deo and Desai, 1999)
- Selection of plant material and processes that yield products with acceptable fastness properties (Aydin and Zeki, 2003; Bechtold *et al.*, 2007)
- Standardization of extraction and dyeing of the plant material (Aydin and Zeki, 2003; Cox and Leslie, 1999)

Solvents play a significant role in textile conservation, including cleaning and dissolving conservation materials (Timar-Balazsy and Eastop, 1998).

From an industrial point of view it would be easier to resort to extracts despite there is at present no definite answer to this prospective solution. The simplest extract would be a watery one although not all the dye pigments are water-soluble. Use of organic solvents might give rise to extracts incompletely water-soluble (De Santis and Moresi, 2007). In principle, it would be much easier for the industrial dyers willing to revive the natural dyeing techniques to replace Osage orange particles with concentrated extracts of its pigments, provided that the solvent chosen guarantees a series of properties as follows:

- Its extraction capacity is extremely high for practically all the natural pigments present in the raw materials of interest
- Its boiling temperature and latent heat of vaporization is quite low to allow its separation at low temperatures with minimum energy consumption
- Its reactivity with colors and pigments is insignificant to avoid any loss in the color quality (De Santis and Moresi, 2007)

The present investigation, therefore, was aimed at identifying the most appropriate leaching solvent for Osage orange pigments to produce an optimum concentrated extract used for dyeing woolen fabric. This has been carried out ultrasonically in comparison with the conventional heating method, using water, in addition to the co-solvents of water-acetone and water-ethanol mixtures at different concentrations, temperature and time intervals.

MATERIALS AND METHODS

This study was taken place via a scientific mission at the School of Chemical and Physical Science, Faculty of Science at Victoria University of Wellington, New Zealand in 2007-2008.

Fabric: One hundred percent mill scoured wool fabric purchased from the New Zealand market, was further scoured with a solution containing 2 g L⁻¹ of each of sodium carbonate and Nonidet

@ P 40 Substitute (Sigma- Aldrich NZ Ltd) at 60°C for 30 min. using a liquor ratio of 50:1. The fabric was thoroughly rinsed in warm and cold water, then left to dry at ambient temperature.

Pigment leaching and estimation of extraction yields: To select the best solvent for Osage orange, distilled water and other co-solvents, such as water-acetone and water- ethanol mixtures all of analytical grade, were tested at concentrations of 10% v/v. Two gram of Osage orange powder (Hands Ashford NZ, LTD, ChristChurch, NZ) was suspended in 20 cm³ of solvent and in a thermostatic bath as well ultrasonic bath at 60°C, for 120 min.

Once water-acetone co-solvent and ultrasonic assisted extraction were chosen as the preferable technique of extraction, 10% w/v Osage orange powder, dissolved in 2.5-25% v/v acetone, at 25- 60°C, for 30-120 min, were carried out to determine the standardization method of extraction.

Dyeing: Ultrasonic assisted dyeing was performed at a liquor ratio of 30:1 for 60 min at 60°C.

After dyeing, the woollen samples were rinsed in cold running water until no more colour was adsorbed and held for stripping with 25% aqueous DMF for 30 min. at 60°C, using a liquor ratio of 50:1, followed by washing-off at a liquor ratio of 50:1, with 2 g L⁻¹ Nonidet @ P 40 Substitute at 60°C, for 30 min. Finally, the samples were rinsed twice in warm and cold water, then left to dry at ambient temperature.

Measurements: The absorbance of Osage orange extract and the reflectance measurements on the dry dyed wool were carried out using Cary 100 UV-Vis Spectrophotometer.

RESULTS

To select the leaching solvent capable of maximizing the extraction yield of Osage orange, several trials were carried out by distilled water and the co-solvents of water-acetone and water-ethanol mixtures at 25-60°C for 30-120 min. The ultrasonic efficiency had been determined simultaneously with the recognized standard procedure of extraction parameters and compared experimentally with the conventional heating method. Practically coincident with that pertaining to water, the yield coefficients for the co-solvents were definitively greater, whether using ultrasonic or the conventional heating method with much higher values in case of ultrasonic. Water-acetone mixture was found to be the most selective co- solvent for extracting the Osage orange dye, followed by water-ethanol and distilled water. As shown in Fig. 1 and 2 water-acetone mixture released over 32% of the total dye absorbency, exhibiting 21% of the total color strength when dyeing the woolen sample. Water-ethanol extracted 27% dye and exhibited 19% color strength, while water extracted less than 21% dye and exhibited 16% color strength. This was relative to 10, 6 and 4% of absorbance and 18, 15 and 11% color strength respectively with the co-ordinate solvents when using the conventional heating method. Figure 3 and 4a, b showed the absorption and color strength values of Osage orange powder extracted by acetone at different concentrations of 2.5-25% v/v at temperatures from 25-60°C, for time intervals varied between 30-120 min. It can be noted that the maximum values were achieved when extracted the Osage orange powder in 20% v/v acetone at 60°C, for 60 min.

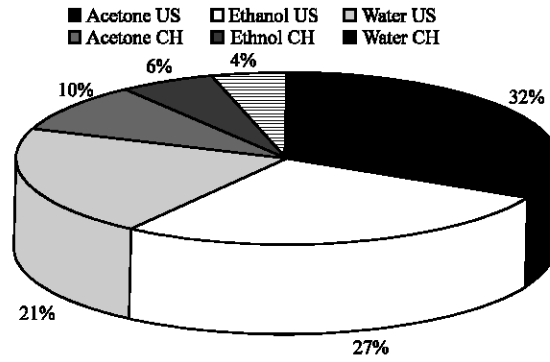


Fig. 1: Effect of solvents on the absorbency of Osage orange powder using the conventional [CH] and ultrasonic [US] assisted extraction

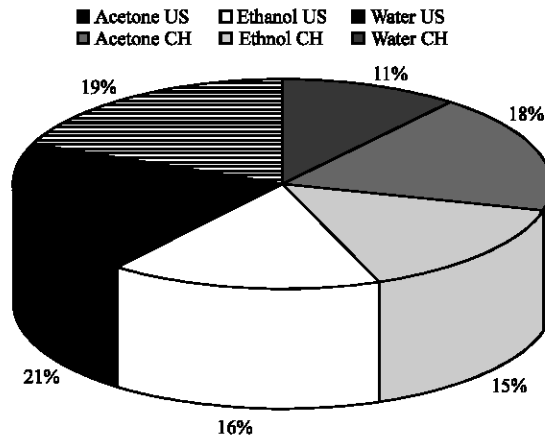


Fig. 2: Effect of solvents on the color strength of Osage orange dyed wool using the conventional [CH] and ultrasonic [US] assisted extraction

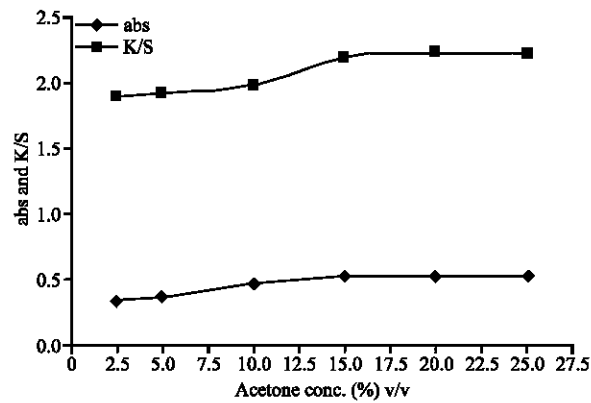


Fig. 3: Effect of acetone concentration on the absorbency and color strength of Osage orange dyed wool using ultrasonic assisted extraction

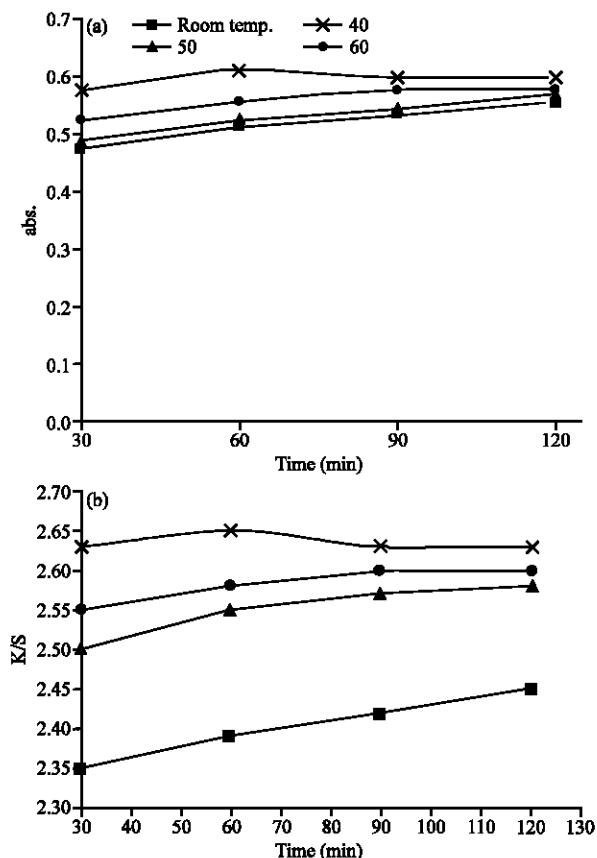


Fig. 4: (a) Effect of ultrasonic assisted extraction time on the absorbency of Osage orange at different temperatures and (b) Effect of ultrasonic assisted extraction time on the color strength of Osage orange dyed wool at different temperatures

DISCUSSION

It is very well known that the extraction parameters affected the color strength of the dyed wool and are influenced by the properties of solvents in which they are carried out.

These include the dipole moment, dielectric constant and refractive index values. The most important property in this regard is the solvent polarity which can change the position of the absorption or emission band of molecules by solvating a solute molecule or any other molecular species introduced into the solvent matrix (Muhammad Rau *et al.*, 2008).

By the way, dye molecules or pigments are complex organic molecules which might carry charge centers and are thus prone to absorption changes in various media (Oliveira *et al.*, 2002; Bevilaqua *et al.*, 2006). These changes are important to understand various physical-organic reactions of these macromolecules which have become important in dye extraction from solution (Hollen *et al.*, 1979).

Acetone acts as the non hydrogen-bond donating solvents (also called as non-HBD type of solvents), while water and ethanol are the hydrogen-bond donating solvents (also called as HBD type solvents) (Muhammad Rau *et al.*, 2008). The absorbency values of Osage orange in these solvents are given in Fig. 1. It can be noted from this figure that the absorption maximum of the extract is affected by the solvent type, thus the change in values can be noted as a probe for various types of interactions between the solute and the solvent.

Water and ethanol are considered as polar protic solvents, their polarity stems from the bond dipole of the O-H bond, whereas the large difference in the electro- negativities of the oxygen and hydrogen atom, combined with the small size of the hydrogen atom, warrant separating the Osage orange molecules that contain the OH groups from those polar compounds that do not. On the other hand acetone considered as dipolar aprotic solvent, containing a large multiple bond between carbon and either oxygen or nitrogen e.g. C-O double bond (Muhammad Rau *et al.*, 2008).

Although water has the highest dielectric constant among ethanol and acetone solvents, its extraction demonstrated the lowest value of absorbency. This might due to the formation of strong hydrogen bond between the dye extract and water molecules (Bruce *et al.*, 2000). The dye absorbance is also influenced by the presence of co-solvents. Water-acetone mixture exhibited the highest value of absorbance, followed by the second water-ethanol mixture. In case water-acetone, the salvation of extract is non-HBD type of solvent mainly occurs through charge-dipole type of interaction, whereas in HBD type of solvent, the interaction also occurs by hydrogen bonding besides the usual ion-dipole interaction. In this situation, the methyl groups of acetone are responsible for the solvation of the dye extract. Thus, decreasing the amount of non-HBD acetone solvent concentration increasing the amount of HBD solvent (water) shall break these interactions with the dye molecule, thereby decreasing the value of absorbance.

Water-ethanol mixtures belong to HBD type of solvents, whereas the dye cation is preferentially solvated by the alcoholic component in all mole fractions in aqueous mixtures with ethanol. It is well known that water makes strong hydrogen-bonded nets in the water-rich region, which are not easily disrupted by the co-solvent (Gomez *et al.*, 2004). This can explain the strong preferential salvation by the alcoholic component in this region since water preferentially interacts with itself rather than with the dye. In the alcohol-rich region, the alcohol molecules are freer to interact with the water and with the dye, since their nets formed by hydrogen bonds are weaker than in water. In this situation, the alcohol molecules can, to a greater or lesser extent, interact with water through hydrogen bonding (Bevilaqua *et al.*, 2006).

Wool fiber is considered as relatively easy fiber to dye, the ease with which the polymer system of wool will take in dye molecules is due to polarity of its polymer and its amorphous nature. The polarity will readily attract any polar Osage orange molecules and draw them into the polymer system. The studies of wool dyeing process have been in two distinct theories (The Gilbert- Rideal's and Donnan theories). The Gilbert and Rideal theory based on Langmuir's theories of surface adsorption, in which the activity coefficient of Osage orange extract ions adsorbed into the wool phase are reduced due to specific binding with sites on wool, which is the formation of ion pairs. This theory proposed that dyeing process is an anion exchange process, in which the Osage orange extract molecules displace smaller anions, depending on four steps: a) diffusion to fiber surface, b) transfer across that surface, c) diffusion within to appropriate sites and d) binding at those sites. On the other hand, according to the Donnan equilibrium theory, the Osage orange extract was considered to partition between the external solution and internal solution phase in the wool. The later phase is believed to contain a high concentration of fixed ionic groups and hence solute molecules have reduced activity co-efficient in that phase due to coulombic interaction, whereas Osage orange is a water soluble dye containing hydroxyl groups that would interact ionically with the protonated terminal amino groups of wool fibres at acidic pH via ion exchange reaction. Reichardt (1994), Kowski (2002) and Gomez *et al.* (2004) as shown in the following scheme.

CONCLUSION

With the demand for more environmentally friendly methods and increasing productivity, the newer ultrasonic energy in assisting the extraction of Osage orange natural dye have been developed, over the conventional heating extraction methods, involving come shorter extraction times and much higher dye absorbance and color strength at lower temperature. Water-acetone co-solvent and ultrasonic have been found to be the suitable alternatives to the conventional water heating method.

The maximum color yield of dye is dependent on solvent polarity. Solvation of dye molecules probably occurs via dipole-dipole interactions in non-hydrogen-bond donating solvents, whereas in hydrogen-bond donating solvents the phenomenon is more hydrogen bonding in nature. The dye uptake depends on (The Gilbert- Rideal's and Donnan theories) depending on the coulombic interaction between the anionic groups (OH) in fact: O⁻ of Osage orange extract and the protonated amino groups of wool fibers.

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