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1. Introduction

Dyeing was known as early as in the Indus Valley period (2600-1900 BC); this knowledge has been substantiated by findings of colored garments of cloth and traces of madder dye in the ruins of the Indus Valley Civilization at Mohenjodaro and Harappa. Natural dyes, dye-stuff and dyeing are as old as textiles themselves. Man has always been interested in colors; the art of dyeing has a long past and many of the dyes go back into prehistory. It was practiced during the Bronze Age in Europe. The earliest written record of the use of natural dyes was found in China dated 2600 BC. [1-4] Primitive dyeing techniques included sticking plants to fabric or rubbing crushed pigments into cloth. The methods became more sophisticated with time and techniques using natural dyes from crushed fruits, berries and other plants, which were boiled into the fabric and which gave light and water fastness (resistance), were developed. After the accidental synthesis of mauveine by Perkin in Germany in 1856 and its subsequent commercialization, coal-tar dyes began to compete with natural dyes. With advances in chemical techniques, the manufacture of synthetic dyes became possible, leading to greater production efficiency in terms of quality, quantity and the potential to produce low-cost raw materials. As a result, natural dyes were progressively replaced by synthetic dyes, whereas over 80% of which is constituted of the aromatic azo type [5] However, researches have shown that synthetic dyes are suspected to release harmful chemicals that are allergic, carcinogenic and detrimental to human health. In addition, textile industries produce huge amounts of polluted effluents that are normally discharged to surface water bodies and ground water aquifers. These wastes cause many damages to the ecological system of the receiving surface water, creating a lot of disturbance to the ground water resources [6-9]. Therefore, in 1996, ironically Germany became the first country to ban certain azo dyes [10].
The world-wide demand for fibers and safety dyes is increasing probably according to the greater awareness of the general consumers in the USA, Europe and Japan towards the highly pollutant procedures affecting fiber and textile coloration when using synthetic dyes which act as a sources of skin cancer, disorders and allergic contact dermatitis [11]. Therefore, interest in returning back to natural dyes as synthetic dyes substitute has increased considerably on account of their high compatibility with environment, relatively low toxicity and allergic effects, as well as availability of various natural coloring sources such as from plants, insects, minerals and fungi [12]

Natural dyes can be obtained from plants, animals and minerals, producing different colors like red, yellow, blue, black, brown and a combination of these. 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 [13]
- supply of dye-houses with the required amount of plant material [13]
- standardization of extraction and dyeing of the plant material [14]
- selection of plant material and processes that yield products with acceptable fastness properties [14]

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 water-y one although not all the dye pigments are water-soluble. Use of organic solvents might give rise to extracts which are not completely water-soluble [15], 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 [15].

Natural dyes are substantive and require a mordant to fix to the fabric, and prevent the color from either fading with exposure to light or washing out. These compounds aid a chemical reaction between the dye and the fiber, so that the dye is absorbed. Traditionally, mordants were found in nature. Wood ash or stale urine may have been used as an alkali mordant, and acids could be found in acidic fruits or rhubarb leaves.

There are three types of mordant: i) Metallic mordants; Metal salts of aluminium, chromium, iron, copper and tin, ii) Tannins; Myrobalan and sumach, iii) Oil mordants; mainly used in dyeing Turkey red color from madder by forming a complex with alum.

In order to obtain high color yield, different shades and good fastness properties, metallic salt mordants are normally employed [16]. The application of mordants for dye fixation was carried
out by three methods; i- Pre-mordanting; dipping the fabric in the mordant solution before dyeing, ii- Simultaneous mordanting; addition of mordant in the dye bath during the dyeing, and iii- post mordanting; dipping the fabric in the mordant solution after dyeing [17].

Osage orange (Maclura pomifera) is a tree in the Moraceae family [18]. 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. It is native to Southern Oklahoma and Northern Texas, and is planted throughout the United States. Several compounds have been isolated and identified in various parts of this tree namely, isoflavonoids from the fruit, flavonols and xanthones from the heartwood and stem bark, and flavanones and xan-thones from the root bark [19] It contains lectins, triterpenes, xanthones and flavone-type compounds such as Scandenone and auriculasin as shown in Figure 1 [20] Two predominant isoflavones, pomiferin and osajin, are derived from the simple isoflavone genistein by prenyl substitutions [21] as shown in Figure 2.

![Figure 1. Chemical structures of scandenone (I) and auriculasin (II)](image1)

![Figure 2. Chemical structures of Osajin (i) and pomiferin (ii)](image2)
The compounds, osajin, iso-osajin, pomiferin, and iso-pomiferin have been characterized and their chemical structures determined. They are isoflavones with the following structures as shown in Figure 3. [19, 21].

![Chemical Structure of isopomiferin](image)

**Figure 3. Chemical Structure of isopomiferin**

As well as Osage orange was applied as an eco-friendly dye acting as one of the environmental problems solutions. New concepts in the cleaner production are being evaluated to solve the high water and energy consumption in textile industries.

The use of ultrasonic as a renewable source of energy in textile dyeing has been increased due to many advantages associated with it [22-25]. Ultrasonic energy represents a promising technique for assisting silk treatment, dyeing, and mordanting processes in comparison with the conventional heating technique. Sonic energy succeeded in accelerating the rate of, dyeing, and mordanting at lower temperatures rather than the conventional heating technique.

Therefore, the present investigation was aimed at identifying the most appropriate leaching solvent for Osage orange pigments to produce an optimum concentrated extract used for dyeing protein fibers; silk and wool fabrics. This has been carried out ultrasonically in comparison with the classical thermal method, using water, in addition to the co-solvents of water-acetone, and water-ethanol mixtures at different concentrations, temperature and time intervals. The optimum condition of the efficiency of ultrasonic assisted dyeing and mordanting methods of Osage orange extraction on the quality of the dyed protein based materials were determined.

### 2. Experimental

#### 2.1. Materials

Degummed and bleached plain Habotain silk fabric, and 100% mill scoured wool fabric purchased from Sherazad Com. New Zealand, were further washed with a solution containing 0.5 g/L of sodium carbonate and 2 g/L of non-ionic detergent (Nonidenet® P 40 Substitute purchased from Sigma- Aldrich NZ. Ltd.), keeping the material to liquor ratio at 1:50, for 30 min. at 40-45°C. The scoured materials were thoroughly washed and dried at ambient temperature. [23]
An analytical grade alum and the commercially cream of tartar were used as mordantas.

2.2. 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. 2 g of Osage orange powder (Hands Ashford NZ, LTD, ChristChurch, NZ) was suspended in 20 cm$^3$ of solvent, and in thermostatic as well ultrasonic baths at 60 $^\circ$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) $^\circ$C, for 30-120 min, were carried out to determine the standardization method of extraction. [24]

2.3. Dyeing and mordanting

1 % Osage orange extract was filtered and used as a dyeing bath. Silk and wool samples were added to the extract, and the dyeing parameters were studied ultrasonically keeping the material to liquor ratio at L: R of 1:30, for time intervals varied between 30-120 min, at temperatures from 30-60$^\circ$C. In terms of the pH used for dyeing; the pH values ranging from (3-11) were carried out to control the dye uptake.

On studying the mordanting methods, the optimum concentration of 8% w/v Osage orange extract was carried out. Stock solutions of 50 gm/ l alum and 25 g/l mixture of each of alum and cream of tartar were prepared. Two different methods of mordanting were used: (1) pre-mordanting method: the samples were first mordanted and then dyed without intermediate washing; and (2) post-mordanting method: the samples were first dyed and then mordanted. Ultrasonic assisted mordanting was carried out in comparison with the conventional heating method at 50-60$^\circ$C, for 90 min, at pH 5. samples were rinsed, washed with 0.5 g/L sodium carbonate and 2 g/L of non-ionic detergent at 40-45$^\circ$C for 30 min, keeping the material to liquor ratio at 1:50. Finally washed with water, and dried at ambient temperature. [23, 26, 27]

2.4. Measurements

Dyestuff content of the dyed fabrics was determined according Kubelka-Munk equation [28] using Cary 100 UV-Vis Spectrophotometer

\[ f(R) = \frac{(1 - R)^2}{2R} \approx \frac{k}{s} \]

R is the absolute reflectance of the sampled layer, K is the molar absorption coefficient and s is the scattering coefficient.

After which the samples were tested for color fastness to light and washing according to AATCC107-1997 [29] The CIE-Lab values of the dyeings were measured and the cylindrical co-ordinates of color were determined after exposure to arc lamp irradiation for 1, 2, 4, 6, 24, 48, and 72 hrs. The colors are given in an internationally commission (CIE L*a*b*) coordi-
nates, L* corresponding to brightness, a* to red–green coordinate (positive sign = red, negative sign = green) and b* to yellow–blue coordinate (positive sign = yellow, negative sign = blue). [30-32].

\[
\Delta E_{ab}^* = \left\{ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right\}^{1/2}
\]

3. Results and discussion

3.1. Extraction parameters

Extraction was carried out by water, water-acetone, and water-ethanol mixtures at 25-60 °C for 30-120 min. The ultrasonic efficiency had been determined simultaneously with extraction parameters, and compared with the conventional heating method. The yield coefficients of co-solvents were definitively greater than water, with much higher values in case of ultrasonic. Water-acetone mixture was found to be the most selective co-solvent followed by water-ethanol. As shown in Figures [4, 5] 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 4](image)

Figure 4. Effect of solvents on the absorbency of Osage orange powder using the conventional [CH] and ultrasonic [US] assisted extraction

Figures 6, 7 and 8 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.

The maximum values were achieved with 20 % v/v acetone at 60° C, for 60 min. The extraction parameters affected the color strength and are influenced by the properties of solvents such as, the dipole moment, dielectric constant, and refractive index values.
The solvent polarity 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 [33]. By the way, dye molecules are complex organic molecules which might carry charge centers and are thus prone to absorption changes in various media [33, 34].

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) [33]. The absorbency values of Osage orange in these solvents are given in Figure 4, 5. It can 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. [33-35].

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 dyes extract and water molecules [33-35].

![Figure 7. Effect of ultrasonic assisted extraction time on the absorbency of Osage orange at different temperatures](image-url)
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 [33, 34]. 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 [33-35].

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 [36], 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 between the anionic groups (OH) in fact: O of Osage orange extract and the protonated amino groups of wool. [36]

Figure 9. Effect of Osage orange concentration (w/v)%, extracted ultrasonically in 20 % water/ acetone co-solvent at 60 °C for 90 min, on the color strength of silk and wool samples.

Higher color depth was expected from an increase in the extract concentration and the use of high concentrations of mordant [37]

To study the possibility of forming concentrated extracts, different amounts of Osage orange bark powder (1-10) g were extracted per the optimized 20 % water/ acetone co-solvent. The dyeing process was carried out on silk and wool samples at a liquor ratio of L: R 1:20, for 60 min. at 60 °C. It was noted that, the use of more concentrated extracts resulted in somewhat
an increase in color depth; whereas the maximum color depth was achieved with 8% w/v powder on both fabrics as shown in Figure 9. The relative high K/S values for dyeings can be explained with the high amount of bark extracted for this series of dyeing experiments.

3.2. Dyeing parameters

Dyeing temperature and time are important parameters influencing the quality of the dyed silk and wool samples. It is well known that dyeing at high temperature for a long time tends to decrease the fabric strength. [36-38] Therefore, it was proffered to dye the samples ultrasonically at temperatures ranging from 30 to 60 °C, relative to the dyeing time that was studied from 30 to 120 mins.

As shown in Figures 10 and 11, it is clear that the standard parameters of dyeing temperature and time were achieved after 90 mins, at 40 – 50 °C, and 50-60 °C in case of silk and wool respectively, where the color strength increases with the increase in dyeing temperature.

Generally, the increase in dye-uptake can be explained by the fiber swelling which enhanced the dye diffusion. [37] The effect of dyeing time was conducted to reveal the effect of power ultrasonic on the de-aggregation of dye molecules in the dye bath. It was denoted that the color strength obtained increased as the time increased. The decline in the dye-ability may be attributed to the hydrolytic decomposition of the extract molecules under the influence of sonic energy during prolonged dyeing. [38]

Figure 10. Effect of dye bath temperature at different time intervals on the color strength of silk samples dyed ultrasonically with 1% (w/v) Osage orange extract.
As shown in Figures 12 and 13 the pH values of the dye bath, have a considerable effect on the dyeability of silk and wool fabrics with Osage orange extract under ultrasonic. As the pH increases the dyeability decreases. The effect of dye bath pH can be attributed to the correlation between dye structure and the protein based materials.

Since the used dye is a water-soluble dye containing hydroxyl groups, it would interact ionic-ally with the protonated terminal amino groups of silk and wool fibers at acidic pH via ion exchange reaction.

The anion of the dye has a complex character, and when it is bound on fiber, further kinds of interactions take place together with ionic forces. This ionic attraction would increase the dye-ability of the fiber as clearly observed in Figures 12 and 13. At pH greater than 5, the ionic interaction between the hydroxyl anion of the dye and the protein fibers decreases due to the decreasing number of protonated terminal amino groups of silk and wool and thus lowering their dye-ability. It is to be mentioned that the lower dye-ability may be attributed to the enhanced desorption of the dye as its ionic bond is getting decreased [36].
Figure 12. Effect of the dye bath pH on the color strength and wave length of silk samples dyed ultrasonically with 1% Osage orange at 40-50°C for 90 min.

Figure 13. Effect of the dye bath pH on the color strength and wave length of woolen samples dyed ultrasonically with 1% Osage orange at 50-60°C for 90 min.

3.3. Mordanting methods & colour properties

As shown in Figures 14 and 15, ultrasonic [US] assisted mordanting method possesses a remarkable improvement in the color strength, in comparison with the classical thermal meth-
The obtained dyeings are governed by the descending dyeing sequence, and can be ranked as follows: pre-mordanting with a mixture of alum and cream of tartar followed by dyeing > post mordanting with alum > post mordanting with a mixture of alum and cream of tartar > premordanting with alum > unmordanted samples.

Silk and wool fabrics are highly receptive to mordants due to their amphoteric nature; they can absorb acids and bases with equal effectiveness. Mordants during natural dyeing, exhibit its fast color due to their complex formation with the dye and fiber [27, 38].

It is clear that: (i) pre-mordanting with the nominated mordant brings about a significant enhancement in the K/S values of the obtained dyeings. (ii) the extent of improvement is governed by the physical and chemical states of the dye and degree of fixation, (iii) premordanting followed by dyeing gives dyeings with better fastness properties than those dyed without mordant and mordanting after dyeing (iv) the improvement in the dyeings color strength and fastness, reflects higher extent of dye adsorption, interaction and bridging with the pre-mordanted substrate via different conjugated bonds [27].

The low color strength in post-mordanting condition is due to the accumulation of the metal dye complex in form of clusters. [39]. The high aluminum content might provide useful eco-friendly chelating with Osage orange molecules presented in the extract that might resist their hydrolysis by water. [39]

The commercial cream of tartar (Potassium Bitartrate) contains a small percentage of calcium tartrate is frequently employed as a mordant for wool. [40]. In this study it was recommend-
ed to apply cream of tartar with alum as preferable mordant to get good strong colors as discussed previously. It helps to soften fibers when alum is used, and can also help brighten the yellow color with good levelness. [40]

Figure 15. Effect of mordant and mordanting method on the color strength of wool dyeings

Sonic energy succeeded in accelerating the rate of mordanting at lower temperatures rather than the conventional heating technique. The exhibited improvement was generally attributed to the acoustic cavitation, which is the formation of gas-filled micro-bubbles or cavities in a liquid media, producing implosive collapse, which often forming fast-moving liquid jets, where large increases in temperature and pressure are generated. The micro-jets increase the diffusion of solute inside the intermediate spaces of silk and wool fabrics facilitate the de-aggregation of Osage orange molecules in the dye bath and thus increase the dye diffusion rate, and penetration through the fibers. [22-24, 41]

A variety of color hues were obtained with respect to the mordant. It was observed from the color fastness data that the extracted dye from Osage orange furnished different color hues with very good affinity for silk and wool fabrics in presence of alum and cream of tartar mordant as illustrated in Tables 1 and 2. The color intensity reached its highest value when the fabrics treated with a mixture of alum and cream of tartar. The brightness of the shades on the dyed samples might be due to the better absorption of Osage orange extract and the easy metal complex formation of mordant with the fibers. Data represented good to very good fastness to washing, because the mordant lead to the formation of a complex dye which aggregates the dye molecules into a large particles insoluble in water. Control samples exhibited poor fastness to washing due to the weak dye- fiber bond, and the ionization of the (OH) groups of the dye during washing under the alkaline condition. [42-45]
<table>
<thead>
<tr>
<th>Samples</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>Wash fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank US</td>
<td>54.12</td>
<td>4.71</td>
<td>49.2</td>
<td>3</td>
<td>5</td>
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<tr>
<td>alum CH</td>
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<td>3.57</td>
<td>43.37</td>
<td>3-4</td>
<td>5-6</td>
</tr>
<tr>
<td>alum US</td>
<td>55.05</td>
<td>3.56</td>
<td>51.67</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
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<td>3.81</td>
<td>37.31</td>
<td>4</td>
<td>6-7</td>
</tr>
<tr>
<td>Alum + cream of tartar US</td>
<td>50.29</td>
<td>6.43</td>
<td>44.8</td>
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<td>6-7</td>
</tr>
<tr>
<td>alum CH</td>
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<td>4.83</td>
<td>48.08</td>
<td>3-4</td>
<td>6</td>
</tr>
<tr>
<td>alum US</td>
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<td>5.40</td>
<td>52.12</td>
<td>3-4</td>
<td>6</td>
</tr>
<tr>
<td>Alum + cream of tartar CH</td>
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<td>3.96</td>
<td>38.21</td>
<td>3-4</td>
<td>6</td>
</tr>
<tr>
<td>Alum + cream of tartar US</td>
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<td>5.52</td>
<td>47.49</td>
<td>3-4</td>
<td>6</td>
</tr>
</tbody>
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Table 1. The CIELab values and fastness properties of Osage orange dyed silk

<table>
<thead>
<tr>
<th>Sample</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>Wash fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.02</td>
<td>55.19</td>
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<td>5</td>
</tr>
<tr>
<td>alum CH</td>
<td>65.07</td>
<td>-0.59</td>
<td>60.08</td>
<td>3-4</td>
<td>5-6</td>
</tr>
<tr>
<td>alum US</td>
<td>67.46</td>
<td>-2.93</td>
<td>62.40</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
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<td>65.43</td>
<td>-0.14</td>
<td>56.89</td>
<td>4</td>
<td>6-7</td>
</tr>
<tr>
<td>Alum + cream of tartar US</td>
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<td>52.60</td>
<td>4</td>
<td>6-7</td>
</tr>
<tr>
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<td>0.68</td>
<td>62.40</td>
<td>3-4</td>
<td>6</td>
</tr>
<tr>
<td>alum US</td>
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<td>1.56</td>
<td>58.98</td>
<td>3-4</td>
<td>6</td>
</tr>
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<td>60.72</td>
<td>3-4</td>
<td>6</td>
</tr>
<tr>
<td>Alum + cream of tartar US</td>
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<td>1.23</td>
<td>55.29</td>
<td>3-4</td>
<td>6</td>
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</tbody>
</table>

Table 2. The CIELab values and fastness properties of Osage orange dyed wool
In the light fastness test, mordanted colored samples exhibited better light fastness relative to the control ones. This may be due to: i) the aluminum metal in alum mordant protects, both by the steric and electronic effects of the weak point in the dye structure from attack by means of the reactive species during photochemical reaction, in addition ii) the aluminum metal in alum mordant promotes aggregation of the dye. By the way, the poor light fastness is due to the inherent susceptibility of the dye chromophore to the photochemical degradation. [46-51]

The colorimetric data indicated the depth and natural tone of the control and mordanted dyed samples. The $L^*$ values were found to be lower using alum and cream of tartar as mordant corresponding to deeper shades. The $L^*$ values were found to be higher in case of unmordanted dyed samples corresponding to lighter shades. Similarly, by using alum as mordant the $L^*$ values were also higher corresponding to lighter shades. The higher values of $a^*$ and $b^*$ indicated the brightness, representing the redness and yellowness hues respectively. As a result, alum and cream of tartar might be effectively used as mordant for Osage orange extract.

The light fading of the dyed samples was recorded in terms of the color difference ($\Delta E$) as shown in Figures 16-20. It was denoted that sonic energy assisted alum and cream of tartar mordanting method, exhibited a lower degree of fading in comparison with the conventional heating and the application alum mordant in absence of cream of tartar, whereas the pre-mordanting method appears to be preferred having a great efficiency in lowering the degree of fading in comparison with the post mordanting.

The dye physical state is generally important than the chemical structure in determining the color fastness on fibers. (31). It was recognized that the light fastness of many dyed systems has been found to increase with the increase dye concentration applied to the substrate [50].

The fiber swelling was increased with ultrasonic technique due to the sonic energy which i) improves the diffusion and penetration of the dye and mordant molecules inside the pores of the fabric, and ii) the fast breaking-down of the dye molecules, which became much more smaller in size and thus fully dispersed with much higher amount in the dyed samples relative to the samples subjected to the conventional heating method, resulted in, the lower degree of fading in case of ultrasonic assisted dyeing and mordantinting processes. [22-25, 41]

Mixture of alum and cream of tartar mordant renders the dye more bonded and more aggregated onto fibers, therefore the surface area of the dye accessible to light is reduced, and thereby the dye fades at lower degree with nearly constant rate of fading.

Aluminum ions apparently produce metal chelates with improved the overall fastness properties. This either could be evidence of the aggregation of dye molecules within the fiber or perhaps of the formation of dye-metal chelates that forms grater stability of the dye molecules when co-ordinated with the complex aluminum metal atom that might form quite large aggregates giving the highest light fast with the lowest fading degree. [23, 51], resulted in, the low and nearly constant fading rate in case of the mordanted samples.
Figure 16. Effect of Xenon arc lamp exposure time on the color retained of silk and wool blank dyed samples.

Figure 17. Effect of Xenon arc lamp exposure time on the color retained of the premordanted dyed silk samples.
Figure 18. Effect of Xenon arc lamp exposure time on the color retained of the post mordanted dyed silk samples

Figure 19. Effect of Xenon arc lamp exposure time on the color retained of the pre-mordanted dyed wool samples
4. Conclusions

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, possessing a 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.

This research demonstrated the standardization dyeing parameters of Osage orange natural yellow extract on protein based fabrics; silk and wool. The color strength increases with the increase in dyeing temperature and time due to the fiber swelling which enhanced the dye diffusion. The effect of dyeing time was conducted to reveal the effect of power ultrasonic on the de-aggregation of dye molecules in the dye bath. The decline in the dye-ability may be attributed to the hydrolytic decomposition of the extract molecules under the influence of
sonic energy during prolonged dyeing. Osage orange is a water-soluble dye containing hydroxyl groups that interacts ionic-ally with the protonated terminal amino groups of silk and wool fibers at acidic pH 5 via ion exchange reaction. The lower dye-ability at pH greater than 5 may be attributed to the enhanced desorption of the dye as its ionic bond is getting decreased. Improvement in the dyeing color strength and fastness properties reflects the higher extent of dye adsorption, interaction and bridging with the pre-mordanted dyed samples via different conjugated bonds with the mixture of alum and cream of tartar mordant. The low color strength in post-mordanting method is due to the accumulation of the aluminum metal dye complex in form of clusters. Sonic energy succeeded in accelerating the rate of mordanting at lower temperatures rather than the conventional heating technique due to the acoustic cavitation which increases the diffusion of solute inside the intermediate spaces of silk and wool fabrics, facilitating the de-aggregation of Osage orange molecules in the dye bath and thus increases the dye diffusion rate, and its penetration through the fibers. A variety of hues were obtained with respect to the mordant. It was observed from the color fastness data that the extracted dye from Osage orange furnished different color hues with very good affinity for silk and wool fabrics in presence of a mixture of alum and cream of tartar mordant. Mordanted dyed samples exhibit better wash and light fastness, with a lowest degree of photo fading relative to the control ones.

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