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# Optimization of Leather Dyeing using Natural Dye Extract

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**Abstract:** ***Consideration of environmentally friendly manufacturing process and product become indispensable issue due to increased environmental and health consciousness. In this regard many nations in the globe have stringent rules and regulations for industrial manufacturing and products to be safe both for environment and human health. Leather is animal skin widely used for footwear, garment, household and technical products. Leather products are colored with synthetic dyes of which, their processing have impact on environment and human health. Hence, the use of nonallergic and nontoxic natural dyes for leather coloration is a matter of significant importance as an option of dye source. The extract from the plant botanically called Osyris Quadripartita and Qerete locally used traditionally for leather dyeing in Ethiopia and other East Africa countries. In this research work, extracting and dyeing conditions were optimized to widen the application of the Osyris Quadripartita plant as a natural dye source for leather dyeing. Extraction was carried at variation of dye material concentration, extraction time and extraction temperature. The largest absorbance (A) value was obtained for dye extracted from 100 g/L dye material concentration, at boiling of 100$^{o}$C for 60 minutes. Dyeing experiments were carried out with and without mordant. Pre and post mordant dyeing techniques were used. The dyed leather samples were analyzed for color strength (K/S), color difference (L*a*b* values) and color fastness properties. The highest color strength (K/S) value was obtained for leather sample dyed with post-mordant method using 2.5% of alum on weight of leather sample. The higher light fastness and rubbing fastness were obtained for leather samples dyed without mordant compared to mordant dyed leather samples. This implies that the extract from Osyris Quadripartita plant has a potential to be an alternative dye source for leather coloration.***

**Keywords:** Natural dye, Leather, Mordant, Mordant dyeing, Color strength, Color fastness

## 1. Introduction

Leather processing and footwear industries are among the important light manufacturing industries which provide ample job opportunity for the younger nation and support economic development of the countries involved in the sector. Particularly this economic sector is significantly important for developing countries as a means of transforming agriculture based economy to industrial economy. Leather is used for producing a range of products from semi and fully processed leather, which include shoe uppers, leather garments, upholstery, backpacks, purses, industrial gloves, finished leather, etc.

For leather good products mainly synthetic dyes are used for imparting color [1, 2]. However, the use of synthetic dyes led to environmental pollution, since toxic substances are involved in their production and effluent discharged after imparting color, which causes carcinogenic, allergic, etc., effects. Now-a- day's manufacturing process and the manufactured product have to be environmentally friendly and safe to human health. This is controlled by stringent rules and regulations set by state of the nations in the world. Therefore, researchers are attempting to have environmentally friendly manufacturing processes and products to be more practiced in manufacturing industries.

Presently, the use of synthetic dyes is estimated at around 10 million tons per annum [3]. The production and application of this large quantity of dye release considerable amounts of waste and unfixed colorants causing serious health hazards and disturbing the eco-balance of nature [4, 5].The increase in environmental awareness has resulted in the imposition of strict eco-standards by many countries in response to noxious reactions associated with synthetic dyes [6]. As a consequence there has been an increase in demand for natural dyes in the past few decades [7].

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources roots, berries, bark, leaves, and wood and other organic sources such as fungi and lichens, timber and food industry wastes [8]. Natural dyes are widely used in the coloring of food, textile, and leather as well as wood products. Traditionally, they were the only colorants for textile fibers like wool, silk, cotton and flax. Their use in textiles has been declined drastically with the introduction of synthetic dyes in 1856 [9]. However, natural dyes are not readily available because of very few organized manufacturers and no standardization of raw material and manufacturing processes. The complex application process also hinders the common use of natural dyes.On the other hand, still natural dyeing practice exists in many countries of the world after more than 160 years of the invention of synthesis dyes. Mostly the extracts of plants are using, for traditional natural dyeing practices in many parts of the world.

This research work is aimed to optimizing the extraction and dyeing conditions of plant which botanicallycalled Osyris Quadripartita and 'Qerte'locally in Ethiopia. The dye extract from OsyrisQuadripartita plant used for dyeing traditionally made baby care leather used for back holding of child called Ankelbain Ethiopia. OsyrisQuadripartita plant is the evergreen shrubs or trees belonging to the sandal wood family, Santalaceae. Osyris compress is a fast growing shrub to a small bushy tree of 1–5 meters in height. It is a partial parasite (hemiparasitic) on the roots of other plants with a smooth grayish bark [10]. The plants are widely distributed in the tropical and temperate regions and it used for extracting, tannin or natural dye. The fresh leaves of Osyris compressa were used to tan leather a light brown color, while the bark was used to tan leather dark brown. Extraction of fresh leaves was used to tan cotton, fishing lines and nets to make them more durable in the days before nylon [10].

This research work focuses on optimizing extraction and dyeing conditions for Osyris Quadripartita plant extract applying standard methods and procedures with standard laboratory equipment. After dyeing with and without mordant, the absorbed and fixed dye was evaluated for color strength (K/S), color difference and color fastness.

## 2. Materials and Methods

### a) Materials

Chrome tanned sheep crust leather was used to carry out the dyeing trials. Osyris Quadripartita plant leaves were collected from Addis Ababa area (central part of the Ethiopia) for extraction of dye. Nonionic wetting agent of 1 % was applied for emulsifying and rehydrating the leather goods. Leather samples were softened and subjected to treatment with 1% of fat liquor to increase flexibility. Formic acid was used as fixing agent. Alum ($KAl(SO_4)_2.12H_2O$) and ferric sulphate ($Fe_2(SO_4)_3$ or iron III were used as mordant.

### b) Equipment

Disk mill was used for powdering sun dried leaves of Osyris Quadripartita plant for extraction. Laboratory drum dyeing machine and oven dryer were used respectively for leather sample dyeing and drying. Solar-box and crock-meter were used respectively for evaluation of light and rubbing fastness of dyed leather samples. For maximum absorbance determination UV-Visible absorbance spectrophotometer was used. The dyed sample color strength and color differences were measured using spectrophotometer.

### c) Methods

#### 1) Dye Extraction

The collected leaves of Osyris Quadripartita plant was dried by exposing to sunlight. The dried leaves were grinded and sieved with 0.5 mm sieve size to obtain the fine powder dye material. Powdered dye material was conditioned at room temperature for 24 hours. The aqueous extraction of dye was carried out from powder dye material with variation of *concentration*, *temperature* and *time* as described here below.

- Concentration: 20 g/L, 60 g/L& 100 g/L;
- Temperature: 60$^o$c, 80$^o$c& 100$^o$c;
- Time: 30 min, 45min & 60 min.

After extraction of dye with stated conditions, the optical density or absorbance value of the extracted dye was measured at wavelength of maximum absorbance ($l_{max}$) using UV-Visible absorbance spectrophotometer.

#### 2) Dyeing

Sheep skin crust leather was first weighed; washed with fat liquored and dyed with dye extracted with various conditions of extraction. Dyeing was carried out with and without mordant. Then, fat liquored and fixation process continues using formic acid and finally the dyed leather sample was subjected to washing and drying processes.

First dyeing was carried out without mordant at 60$^o$Ctemperature for 50 minutes, to justify Osyris Quadripartite plant has a potential to be as natural dye source for leather dyeing. Later dyeing was carried out with optimized conditions of *dye material concentration*, *pH*, dyeing *temperature* and dyeing *time*. Then color strength, color difference and color fastness properties were evaluated for leather samples dyed with optimized dyeing conditions both with and without mordant.

#### 3) Mordant Dyeing

Mordant dyeing was carried out, using the pre and post mordanting methods with 2.5% alum and ferric sulphate (iron III) mordants[11].

#### 4) Color Fastness

For color fastness test, sample was cut from the dyed leather and conditioned at temperature of 20 ± 2$^o$C and 65 ± 2 % relative humidity for a period of 48 hours [11].

#### 5) Color Fastness to Rubbing

Dyed leather samples were subjected to both dry and wet rubbing fastness tests on crock meter and extent of color fading was checked using grey scale reading within ASTM D 5053- 03 (2015) standards with rating scales from 1 to 5, with 5 being 'very good' and 1 being 'poor' respectively [5,11].

#### 6) Color Fastness to Light

The color fastness of dyed leather sample to an artificial light source, Xenon lamp, was measured using standard method (ASTM D 3424- 11). One side of the leather was exposed to light from a Xenon arc under prescribed conditions. Along with dyed eight blue wool standards having increasing levels of fastness. Black panel temperature and the relative humidity are maintained according to the standards. The change in color was compared with the controlled specimen (unexposed to light) and evaluated using ASTM grey scale for change in color. Fastness was assessed by comparing the fading of crust leathers with blue scale standards, ranged from 1 to 8, which 1 and 8 indicates very low and very highlight fastness properties respectively.

### d) Color Strength and Color Difference

Color Strength (K/S) and Color Difference (CIE L*a*b*) were measured using Gretag Macbeth Color Eye 3100 laboratory Spectrophotometer unit Module CE 3100 keeping D65 illuminant and 10$^0$ observer. Higher the color strength implies higher K/S value. Color intensities(K/S) were determined at maximum dye absorption wave length of $l_{max}$ using Kubelka-Munk equation.

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

Where, *K* is the light absorption coefficient, *S* is the light scattering coefficient while *R* is Reflectance value. The L*, a*, b* color space describes mathematically all perceivable colors in the three dimensions that L* for lightness and a* and b* for the color components green – red and blue – yellow respectively. The evaluation was done for leather samples dyed with and without mordant.

**e) Optimizing Conditions for Extraction and Dyeing**

**1) Optimizing Conditions for Extraction**

The variables of *temperature*, *time* and dye *concentration* were considered as important conditions for extraction. The three levels of experimental design were used for each variables following Taguchi Orthogonal Array method. The experimental design was performed using software called Minitab 17. This approach was helped the optimization to be carried out with nine experiments as illustrated Table 2.1. The extraction was carried out with all considered extraction variable matches and the best variable matched that yield high dye concentration was identified after measuring the absorbance of the extracted dye. Then dye extracted with high concentration (high absorbance) was used for dyeing the leather samples.

**Table 2.1:** Optimization of extraction conditions

| Test No. | Dye material concentration (g/L) | Temperature (° C) | Time (minute) |
|---|---|---|---|
| 1 | 20 | 100 | 30 |
| 2 | 100 | 60 | 60 |
| 3 | 100 | 60 | 30 |
| 4 | 100 | 100 | 60 |
| 5 | 20 | 100 | 60 |
| 6 | 60 | 80 | 45 |
| 7 | 20 | 60 | 60 |
| 8 | 100 | 100 | 30 |
| 9 | 20 | 60 | 30 |

**2) Optimizing Conditions for Dyeing**

Dyeing time and dyeing temperature were considered as variables for dyeing conditions optimization as described underneath.

- Time variable: 40 min., 50 min., and 60 min.;
- Temperature: 30°C, 45°C&60°C [11-14].

Dyeing was carried out with mordant and without mordant. Mordant dyeing was carried out using 2.5 % of alum ($KAl(SO_4)_2.12H_2O$) and ferric sulphate $Fe_2(SO_4)_3$ as mordant separately for one hour at 60°C [11]. Dyeing without mordant was also carried out with similar dyeing conditions expect the absence of the mordant. Leather samples dyed without mordant were used for comparison of color strength, color difference and color fastness properties of leather samples dyed with addition of mordant. The best matches of dyeing variables were selected as an optimized dyeing conditions based on high value of color strength (K/S value) measured from dyed leather sample.

**Table 2.2:** Optimization of dyeing conditions

| Test No. | Temperature (° C) | Time (minute) |
|---|---|---|
| 1 | 100 | 30 |
| 2 | 60 | 60 |
| 3 | 60 | 30 |
| 4 | 100 | 60 |
| 5 | 100 | 60 |
| 6 | 80 | 45 |
| 7 | 60 | 60 |
| 8 | 100 | 30 |
| 9 | 60 | 30 |

## 3. Results and Discussions

**a) Optimized Conditions of Extraction**

Dye extraction from Osyris Quadripartita plant was carried out using the extraction parameters given in Table 2.1.The extracted dye was measured for determination of maximum absorbance using UV- visible spectrophotometer after diluting by 1:5 ratios. The results obtained after measurement of the absorbance is depicted in Table 3.1.

**Table 3.1:** Result for optimized extraction conditions

| Test No. | Dye material concentration (g/L) | Temperature (° C) | Time (minute) | A* at 1 486 (nm) |
|---|---|---|---|---|
| 1 | 20 | 100 | 30 | 2.75 |
| 2 | 100 | 60 | 60 | 2.50 |
| 3 | 100 | 60 | 30 | 4.50 |
| 4 | 100 | 100 | 60 | 5.00 |
| 5 | 20 | 100 | 60 | 2.74 |
| 6 | 60 | 80 | 45 | 2.49 |
| 7 | 20 | 60 | 60 | 0.55 |
| 8 | 100 | 100 | 30 | 0.50 |
| 9 | 20 | 60 | 30 | 1.78 |

A*= absorbance

As shown in column 5 of Table 3.1, the largest absorbance (A) value of 5.0 has been obtained with extraction condition matches described in test No. 4. According extraction conditions of test No.4, dye extracted from 100 g/L concentration, at boiling of 100°C for 60 minutes was considered as the optimized conditions of extraction for Osyris Quadripartita plant. The largest absorbance value indicates that, the extracted dye contains increased concentrations of dye material in aqueous solution. Therefore, the dye extracted with these conditions was used for dyeing leather samples.

**b) Optimized Conditions of Dyeing**

**1) Dyeing without Mordant**

Sheep skin chromed tanned crust leather was used for the dyeing experiment. Dyeing was carried out using the experimental design described in Table 2.2. After dyeing the samples were subjected for drying. Then color strength (K/S) and color difference (CIE L* a* b*) were measured for dyed leather samples using Color Eye 3100 spectrophotometer. As shown in Table 3.2, the maximum color strength (K/S) value of 4.11at wavelength of 480 nm was measured for samples dyed at 60°Cfor 50 minutes. Therefore, the dyeing conditions which yield the maximum

(K/S) value were considered as optimized conditions of dyeing for the Osyris Quadripartita plant extract. The relation between the dyeing *temperature*, *time* and the resulted color strength (K/S) at wavelength of 480 nm was plotted as shown in Fig. 3.1.Accordingly as shown in Fig.3.1 in general with increasing dyeing *temperature and time*, the K/S value is correspondingly increased. This implies that increasing dyeing *temperature* and *time* increases the dye-up or dye ability of leather. However, with increased dyeing temperature, the felting of the leather product might be highly affected.

**Table 3.2**: Result for optimized dyeing conditions

| Test No. | Temperature (°C) | Time (minute) | K/S at λ 486 (nm) |
|---|---|---|---|
| 1 | 30 | 30 | 2.5513 |
| 2 | 30 | 40 | 2.3954 |
| 3 | 30 | 50 | 2.1955 |
| 4 | 45 | 30 | 3.1827 |
| 5 | 45 | 40 | 2.7077 |
| 6 | 45 | 50 | 3.2716 |
| 7 | 60 | 30 | 3.7656 |
| 8 | 60 | 40 | 3.9387 |
| 9 | 60 | 50 | 4.1051 |

The optimized conditions of dyeing of 60°Ctemperature and 50 minutes of time were used for mordant dyeing with alum and Iron III mordants**.**

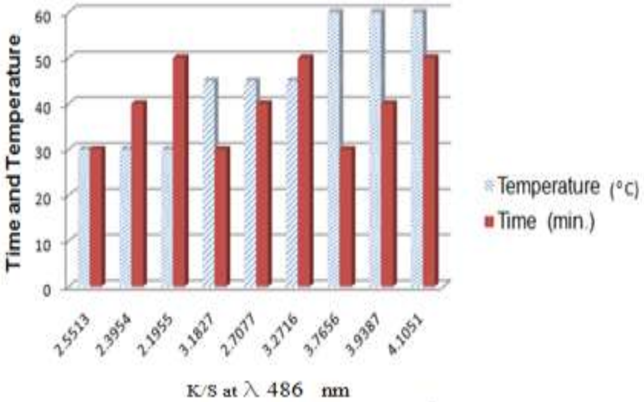


**Figure 3.1**: K/S values versus various dyeing conditions

### 2) Optimized pH media for dyeing

To set an optimum pH condition for dyeing, the pH values were varied from 5.5 to 7.4 with an interval of 0.5, keeping dyeing temperature at 60°C and dyeing time of 50 minutes as shown in Table 3.3.This range of pH is preferred, since most of the leather material is dyed in this range of pH. The maximum color strength (K/S) value of 4.1051 was obtained at wavelength of 480 nm in dyeing at pH value of 6.5, as shown in Table 3.3. So, pH value of 6.5 was considered as optimized medium for dyeing leather without mordant.

**Table 3.3:** Result for optimized pH values

| Test No. | pH | Temperature (°C) | Time (minute) | K/S at λ 486 (nm) |
|---|---|---|---|---|
| 1 | 5.5 | 60 | 50 | 1.0649 |
| 2 | 6.0 | 60 | 50 | 2.9053 |
| 3 | 6.5 | 60 | 50 | 4.1051 |
| 4 | 7.0 | 60 | 50 | 1.6540 |
| 5 | 7.5 | 60 | 50 | 1.7522 |

### 3) Mordant dyeing

Mordant dyeing was carried out with alum and Iron III mordants of 2.5 % weight of leather sample (w.f.l.), at temperature of 60°C for 50 minutes using pre and post mordant dyeing methods.

**Table 3.4:** Result for K/S values for mordant dyed sample

| Mordanting method | Mordant | Mordanting conditions | | K/S at λ 486 (nm) |
|---|---|---|---|---|
| | | Temp.* (°C) | Time (min.) | |
| Pre | Alum | 60 | 50 | 5.2133 |
| Post | Alum | 60 | 50 | 7.3495 |
| Pre | Iron III | 60 | 50 | 3.4851 |
| Post | Iron III | 60 | 50 | 3.8597 |
| Without | No | 60 | 50 | 4.1051 |

Temp*. = Temperature

Color strengths or K/S value of 3.4851 and 3.8597 were obtained for sample dyed with iron III mordant by pre and post mordanting methods respectively. The K/S values obtained for leather sample dyed with iron III mordant both by pre and post mordanting methods are less compared to sample dyed with alum mordant and without mordant as shown in Table 3.4. The K/S value of 4.1051 was obtained for leather sample dyed without mordant, and this K/S value is medium value compared to K/S values obtained for samples dyed with alum and iron II mordans. TheK/S value of 5.2133 and 7.3495 were obtained for sample dyed with alum mordant by pre and post mordant dyeing methods respectively. These K/S values are the highest compared to the K/S values obtained for leather samples dyed with iron III mordant and without mordant. This indicates that dye-up take of leather is increased with alum mordant compared to sample dyed with iron III mordant and without mordant.

As illustrated in Table 3.6 the high L***** value of 50.8, 48.5 and 50.5 were obtained for leather sample dyed by pre and post mordanting methods with iron III mordant and sample dyed without mordant respectively. The high L* value indicates that the dyed sample is lighter in its color (hue).Similarly, the highest **a*** value of 21.0 was obtained for sample dyed without mordant, indicating that the sample dyed without mordant is more redder than the samples dyed with alum and iron III mordants.

**Table 3.5:** The color change with mordant dyeing

| Mordanting method | Mordant | CIE L* a* b* value Observer at 10° with day light (D) | | |
|---|---|---|---|---|
| | | L* | a* | b* |
| Pre | Alum | 37.1 | 4.7 | 4.8 |
| Post | Alum | 29.8 | 1.3 | -0.02 |
| Pre | Iron III | 50.8 | 18.7 | 19.9 |
| Post | Iron III | 48.5 | 16.3 | 18.4 |
| Without | No | 50.5 | 21.0 | 21.6 |

The highest **b*** value of 21.6 was also obtained for leather sample dyed without mordant indicating that the sample dyed without mordant is more yellower in its color compared to samples dyed with alum and iron III mordants. In general the color difference evaluation for leather samples dyed with mordants (alum and iron III) and without mordants shows that the sample dyed without mordant is redder and yellower compared to samples dyed with mordants.

### c) Fastness Evaluation

#### 1) Rubbing fastness

The wet and dry rubbing fastness of leather sample dyed with mordants and without mordants were evaluated, and the result is depicted in Table 3.6.Grade 5 of dry rubbing fastness was obtained for leather sampled dyed without mordant, indicating that Osyris Quadripartita plant extract has very good resistance for dry rubbing fastness without mordant dyeing. On the other hand, the rubbing fastness obtained for leather samples dyed with alum and iron III mordant by pre and post mordant dyeing methods are lower than the rubbing fastness grade of leather sample dyed without mordant as shown in Table 3.6.

**Table 3.6:** Rubbing fastness test result

| Mordanting method | Dry Crok | | Wet Crok | |
|---|---|---|---|---|
| | St | CC | St | CC |
| Pre | 3/4 | 4 | 2 | 3/4 |
| Post | 4/5 | 4/5 | 2 | 3/4 |
| Pre | 4/5 | 4/5 | 2/3 | 4 |
| Post | 4/5 | 4/5 | 2/3 | 4 |
| Without | 5 | 5 | 3/4 | 4 |

St=staining;CC=color change

Similarly, the wet rubbing fastness grade obtained for leather sample dyed without mordant is better both for color change and staining values compared to leather samples dyed with mordant as shown in Table 3.6. In general leather sampled dyed without mordant with Osyris Quadripartita plant extract has high rubbing fastness resistance compared to leather sample dyed in the presence of mordant. This implies that OsyrisQuadripartita plant extract as a natural dye has good substantivity to leather materials with good dye fixation ratio.

#### 2) Light fastness

The light fastness test was performed by exposing the dyed sample for 24 and 48 hours for light source. The result obtained for light fastness is shown in Table 3.7. Blue scale grade 8 is obtained for sample dyed without mordant both for 24 and 48 hours of exposure of dyed sample to light source. The grade 8 of light fastness indicates the excellent resistance property to light. This implies that Osyris Quadripartita plant extract as natural dye has excellent light fastness for leather dyeing even it is difficult to get such a high grade light fastness from most synthetic dyes used for leather dyeing. On the other hand inferior grade of light fastness that is below 5 is obtained for samples dyed in the presence of alum and iron III mordant by pre and post mordant dyeing methods as shown in Table 3.7.

**Table 3.7:** Light fastness test result

| Mordanting method | Light Fastness | |
|---|---|---|
| | 24 hour | 48 hours |
| Pre | 4 | 3 |
| Post | 4 | 4 |
| Pre | 4/5 | 4 |
| Post | 4/5 | 3 |
| Without | 8 | 8 |

Further as shown in Table 3.7long time (48 hours) exposure of dyed leather sample to light source deteriorates the resistance dye for leather sample dyed with mordants.

## 4. Conclusion

The rubbing and light fastness result obtained for leather sample dyed without mordant is very good and commercially acceptable fastness range. The dye from Osyris Quadripartita plant can be well extracted with dye material concentration of 100 g/L at boiling for 60 minutes in aqueous solution. Increased color strength is obtained for Osyris Quadripartita plant extract at 60$^{o}$Ctemperature and 50 minutes of dyeing time without mordant. Dyeing with alum mordant favored for increased color strength both by pre and post mordant dyeing methods. The increased effect of dyeing is obtained at 6.5 of pH for dyeing without mordant.

In general the extract from Osyris Quadripartita plant has a potential for dyeing leather without mordant as per fastness tests results obtained. Dyeing without mordant is preferable for environment and human health safety as well as for reduction of manufacturing cost. The other important aspect of the Osyris Quadripartita plant is it's widely availability in East Africa including Ethiopia for applying as natural dye source for leather dyeing

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