Fibers and Polymers 2016, Vol.17, No.11, 1875-1883
DOI 10.1007/s12221-016-6226-0

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Extraction of Natural Dye from *Coreopsis tinctoria* Flower Petals for Leather Dyeing − An Eco-friendly Approach

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(Received February 11, 2016; Revised March 21, 2016; Accepted October 3, 2016)

Abstract: This study evaluated the extraction of two colors of dye (yellow and brown) from *Coreopsis tinctoria* flower petals using ultrasound and the dyeing of leather with the extracted dyes as a source of nontoxic and eco-friendly dye. The results showed an increase in the dye extraction values with increasing time at 100 W ultrasonic power at 80 °C for 1 h. Leather dyeing was optimized with the aid of ultrasound and magnetic stirring. The optimum leather dyeing conditions, with respect to the dye uptake, dye penetration and intensity of the color, were determined to be 12 % dye concentration, 100 W power, 1,000 rpm, and pH 7.0 for 60 min at 80 °C. It was shown that sonication improves dye exhaustion from a 90 % to 60 % rating for 1 h of dyeing time. The dyed leather was assessed by reflectance measurements and compared with visual assessment data. The fastness properties of dyed leather samples showed good fastness against washing, light, and dry and wet rubbing. The strength properties were not significantly altered and the bulk properties, such as softness, were found to be improved by the use of *Coreopsis tinctoria* yellow and brown dyes using an ultrasonic and magnetic stirring dyeing process.

Keywords: Natural dye, *C. tinctoria*, Ultrasound, Sonochemistry, Leather dyeing

Introduction

In recent years, the textile, cosmetic, pharmaceutical, nutraceutical and other similar sectors have seen a tremendous increase in the use of natural dyes, due to their fascination, applications and adequacy. To impart color to various materials, highly colored substances, called colorants/ dyes or pigments, are widely used [1,2]. During textile/ leather processing, inefficiencies in dyeing result in a large amount of dyestuff being lost directly in the wastewater, which ultimately ends up in the environment. It is estimated that 10-35 % of the dye is lost in the effluent during the dyeing process, while in the case of reactive dyes, as much as 50 % of the initial dye load is present in the dye bath effluent [3,4]. Synthetic colorants have been cited as causing skin complaints, illnesses and cancer [5]. Close skin contact with colored textiles (e.g., leggings heavily dyed with azo and anthraquinone disperse dyes) has become a concern, and some cases of dermatitis have been reported [5]. Many synthetic colorants are classified as toxic when in contact with skin and consumers worldwide require safer clothing products, particularly in the cases of babies and children [6,7].

Natural Dye

Natural dyes have been used since antiquity and are currently emerging as important alternatives to potentially harmful synthetic dyes [1,2,5]. The application of these natural dyes and pigments in the dyeing of cotton, silk and wool samples has been reported in several studies [2,5,8-10]. However, the main disadvantage of these natural dyes lies in the order of magnitude of their extraction yield factors (a few grams of pigment per kg of dried raw material). This makes their current market price about USD 1/g, thus limiting their application to high-value-added natural-colored garments [11]. To overcome this constraint, it may be possible to exploit the potential of plant sources rich in natural dyes. The use of precise dye extraction and application to substrate techniques will likely yield a significant improvement in their potential applications for textile materials.

Coreopsis Tinctoria

Coreopsis tinctoria Nutt., which belongs to the Asteraceae/ Compositae family, is a small, glabrous, aromatic annual plant with a worldwide distribution [12-14]. Locally, it is known as “snow chrysanthemum” or “snow tea” and is traditionally used not only as a tea-like beverage but also in Uyghur folk medicine for the treatment of hypertension and hyperlipidemia [14,15]. Previous studies have shown that *C. tinctoria* flower contains a diverse range of bioactive phytochemicals, including flavonoids [12,16], phenolics [14,17], phenylpropanoids [18], polyacetylene glycosides [19], and sterols [20], with flavonoids being the major phytochemical that is present [21]. The *C. tinctoria* flower has two color shades are brilliant yellow with brown centers (Scheme 1). The brown part is rich in carotenoids compared to yellow lead to difference shades of color. *C. tinctoria* is large quantity of weed in South Korea with flourishing color

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flower and also there is no study till now for leather dyeing using *C. tinctoria* flower pigment, hence we intent to study on leather dyeing using *C. tinctoria* pigment.

Sonicator Dyeing

Sonicator dyeing (SD) has been used to dye cotton [22], silk [23], wool [24,25] and leather [1,2] with various types of natural dye obtained from *Acer Pectinatum wallich, Rubia cordifolia* Linn, *Ixora coccinea*, *Opuntia ficus-indica,* commercial Lac and *Beta vulgaris*, respectively. The cavitation, which occurs near a solid surface, generated by micro jets in the dye bath, facilitates the high speed movement of liquid and gives rise to an increased diffusion of dye molecules inside the fabric pores than any other conventional technique [22]. In the case of sonication, an enhancement in the localized temperature and pressure induces swelling effects in the fiber, thus causing improved diffusion of the dye into the substrate. Leather is a difficult substrate to dye up to a certain level, and achieving a consistent shade due to its unique nature of variations within the leather matrix [26-28]. To achieve the objective of obtaining an even and uniform dyeing level with the maximum uptake of dye, the leather dyer needs to be experienced and have a thorough understanding of the properties of the dyes and any auxiliaries used.

As stated above, several techniques have been used to dye fabric and leather samples with natural dyes. However, the application of *C. tinctoria* petal dyes (yellow and brown color) on a leather sample has not been reported. Hence, the main objective of the present study was to develop a simple and eco-friendly methodology (ultrasound) for dye extraction, as well as for its application for leather. Moreover, the dyeing conditions were optimized and the characteristics of the dyed leather samples were assessed by standard methods.

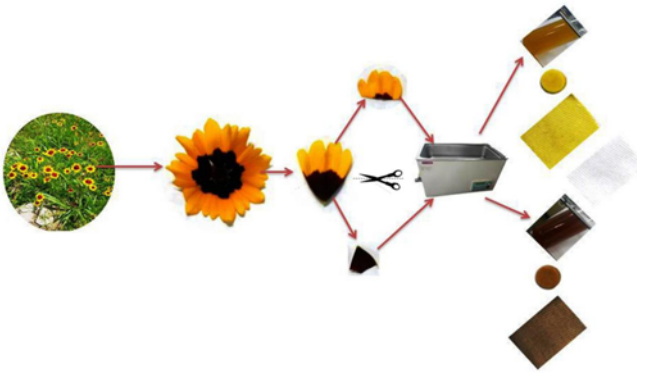
Experimental

Materials

C. tinctoria petals collected in and around Chonbuk National University, Iksan campus, South Korea were used for these experiments. Sterile nanopure water (conductivity= 18 μΩ/m, TOC <3 ppb), (Barnstead, Waltham, MA, USA), was used in this experiment for ecofriendly extraction without any external chemical agent. Ultrasonic (US) water bath treatments were performed using an Ultrasonic bath (SD-D400H, Sonics and Materials, South Korea, 40 kHz and 0-400 W). A conventional chromed wet blue goat leather sample was purchased from an online market in South Korea for further study. The untreated leather sample was used as a control for the subsequent experiments.

Extraction of *C. tinctoria* petals (yellow and brown color) Dye Using Ultrasound

Freshly collected *C. tinctoria* petals were separated into two portions, based on their yellow or brown color, as shown in Scheme 1.



Scheme 1. Showing the *C. tinctoria* plant, flower, separated colors, ultrasonic water bath, flower extract, dyed fabric and paper disc.

Typically, 5 g of each type of separated petal were placed in an extraction beaker along with 50 m*l* of distilled water and then covered with aluminum foil in order to avoid evaporation. The beaker was then placed in the water of the ultrasonic water bath using the preselected values of a fixed temperature inside the galls beaker of 80±2 °C, a working frequency of 40 kHZ, and a maximum input power of up to 400 W with a case volume of 22 *l*. The ultrasonic bath consisted of a rectangular tank with internal dimensions (width×length×height) of 500×300×150 mm^3 and four transducers at the bottom of the bath. In our trials, the time utilized was extended sequentially by 10 min to identify the precise time required for maximum extraction. All experiments were carried out with a 100 m*l* flat bottom glass beaker placed 1 cm above the bottom 15 cm from right to middle of the bath with a liquid height of 7 cm and placed in the middle of ultrasonic bath for the extraction of dye from the *C. tinctoria* petals and for the dyeing of the leather samples. Samples were taken every 10 min and wavelength scanning was performed and recorded at 200-700 nm using a UV-Vis spectrophotometer (Shimadzu, UV-1800, Kyoto, Japan) for up to 60 min. All experiments were performed in triplicate and the average values have been reported with standard deviations.

Leather Dyeing and Optimization

To identify suitable dyeing conditions for the natural dye from *C. tinctoria* by US (ultrasonic water bath) and MS (magnetic stirring), leather dyeing experiments were carried out while varying different parameters. The volume of dye solution in the leather dyeing experiment was calculated to yield a fixed concentration of 12 % dye for all of the dyeing experiments (based on the leather weight). Leather was cut in to 2×2 cm^2 rectangular pieces, as per the (Society of Leather Technologists and Chemists) SLTC 1996 official method of sampling. The upper smooth surface of the leather

was sliced with a sharp knife, washed several times and then air dried. Dyeing was carried out by shaking the leather tad with an optimized concentration of 12 % dye, based on the weight of the leather (owl), in 100 m*l* of deionized water. Several parameters were adjusted to optimize the dyeing conditions using the ultrasonic bath (place positions of leather sample in ultrasonic bath are presented extraction of *C. tinctoria* petals section) and dyeing with magnetic stirring (MS) is in 150, 200, 250, 350, 400, 450 and 500 rpm. The conditions that were varied include the ultrasonic power (20-100 W), magnetic stirring (150-500 rpm), pH (2-10), temperature (40-80 °C), and time (20-190 min). The dyed samples were rinsed with cold water in a bath with a liquor ratio of (*L*:*R*) 50:2 using 3 g/*l* nonionic detergent (laboratory detergent) at 50 °C for 30 min in order to remove the unfixed dye, and then were air dried. The dye bath pH was monitored with a CyberScan pH meter and adjusted with dilute solutions of 1 M sodium carbonate.

Dye Exhaustion in the Process Liquor during Leather Dyeing

The unspent dye in the exhausted process liquor (before and after dyeing) was analyzed using a UV-Vis spectrophotometer at an appropriate scanning wavelength. The percentage of pigment exhaustion was calculated using the following equation:

$$\% \text{ Dye exhaustion} = [(C_g - C_t) / C_g] \times 100 \quad (1)$$

where C_g is the concentration of dye used and C_t is the concentration of dye in the spent liquor.

Analytical Methods

UV-Visible Spectrophotometric Analysis

In order to perform the quantitative analysis of the *C. tinctoria* colorant, the wavelength of maximum absorbance (λ_{max}) for the *C. tinctoria* extract was analyzed using a UV-Vis spectrophotometer. The UV-Visible spectra of *C.*

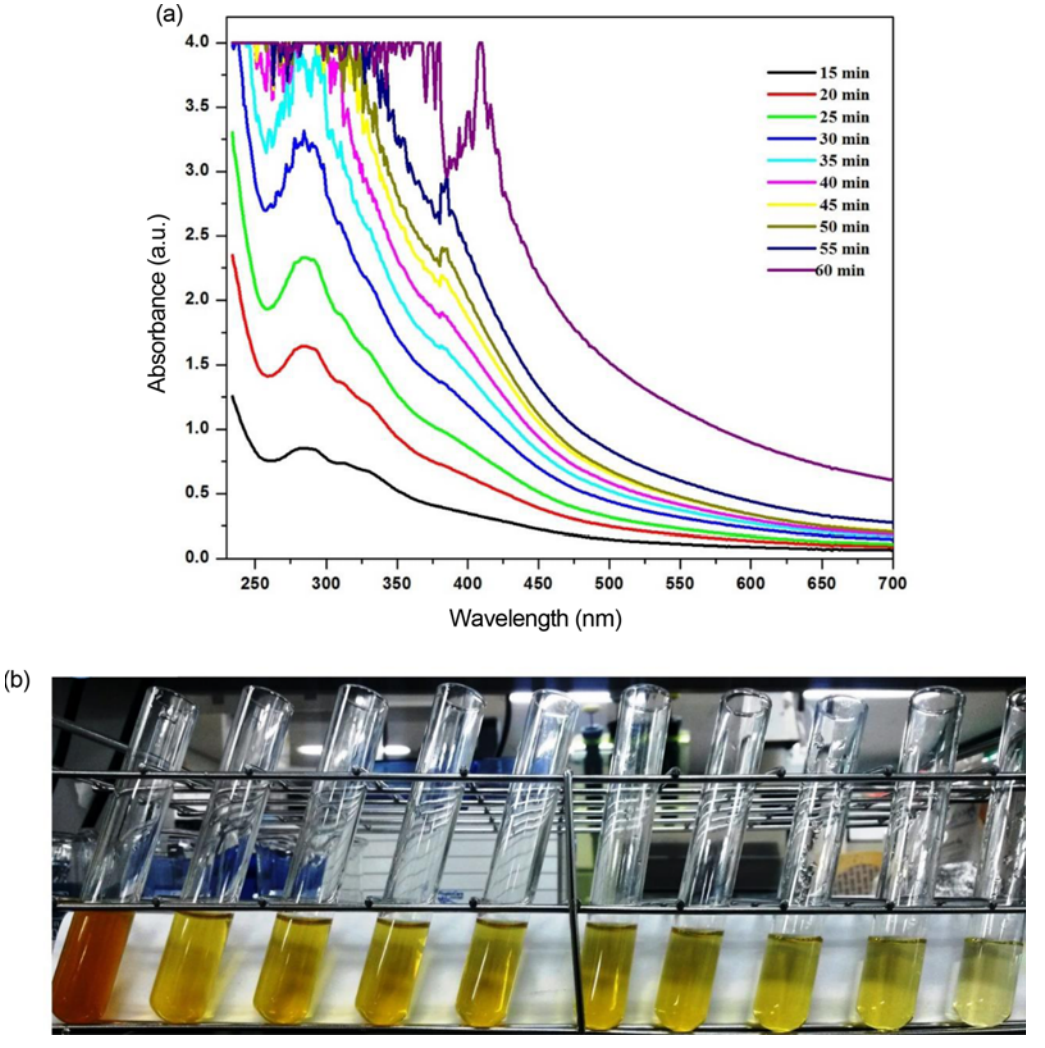


Figure 1. (a) UV-Vis spectrum for *C. tinctoria* yellow dye extraction at different times and scanned wavelengths from 200-800 nm, and (b) visual appearance of the dye at different extraction times.

tinctoria dye extract corresponding to the yellow and brown colors are shown in Figures 1(a), 1(b), 2(a) and 2(b), respectively.

Two peaks were found in each dye at 287 and 479 nm for yellow and at 287 and 433 nm for brown, corresponding to Okanin or 3',5,5',7-tetrahydroxy flavanone, Quercetagetin-7-O-glucoside and Flavanocorepsin, respectively. Figures 1(b) and 2(b) show the dye color and their extraction potential in relation to different time intervals.

Color Measurement Analysis

Quantification of the color of the *C. tinctoria* color dyed leather was performed according to the Commission Internationale de l'Eclairage (CIE) system of color measurement with 10 standard observer data [1,2]. The L^*, a^* and b^* values for both of the grain sides of the dyed leathers were obtained using a Milton Roy ColorMate HDS spectrophotometer, as described earlier [1,2,29]. The values L^*, a^* and b^* are variables in the CIELAB color space and are explained as follows. A more negative value of L^* denotes a darker shade of the color, while a more positive value of L^* denotes a lighter shade. A more negative value of a^* implies a greener color and a more positive value of a^* implies a redder color. A more negative value of b^* means a bluer color and a more positive value of b^* indicates a yellower color.

Assessment of the Organoleptic Properties and Physical Testing Analysis

The leather samples were also subjected to a visual assessment for bulk properties, such as fullness, grain smoothness, softness, grain tightness, uniformity, and general appearance, by four experienced tanners. The assessment was done on a scale of 0-10 points for each functional property, with higher values indicating a better score for each property. An average rating was calculated for each property. The matched pair leather samples made using control and optimized experimental processes of full skin leathers were used for the physical testing of measurements and the samples were cut from the official sampling position (IUP 2 [30] method). The tensile strength, elongation at break, tear strength and grain crack strength were measured as per IUP 6 [31], IUP 8 [32], and IUP 9 [33] methods [34].

Results and Discussion

It has been recognized for many years that power ultrasound has great potential for application in the

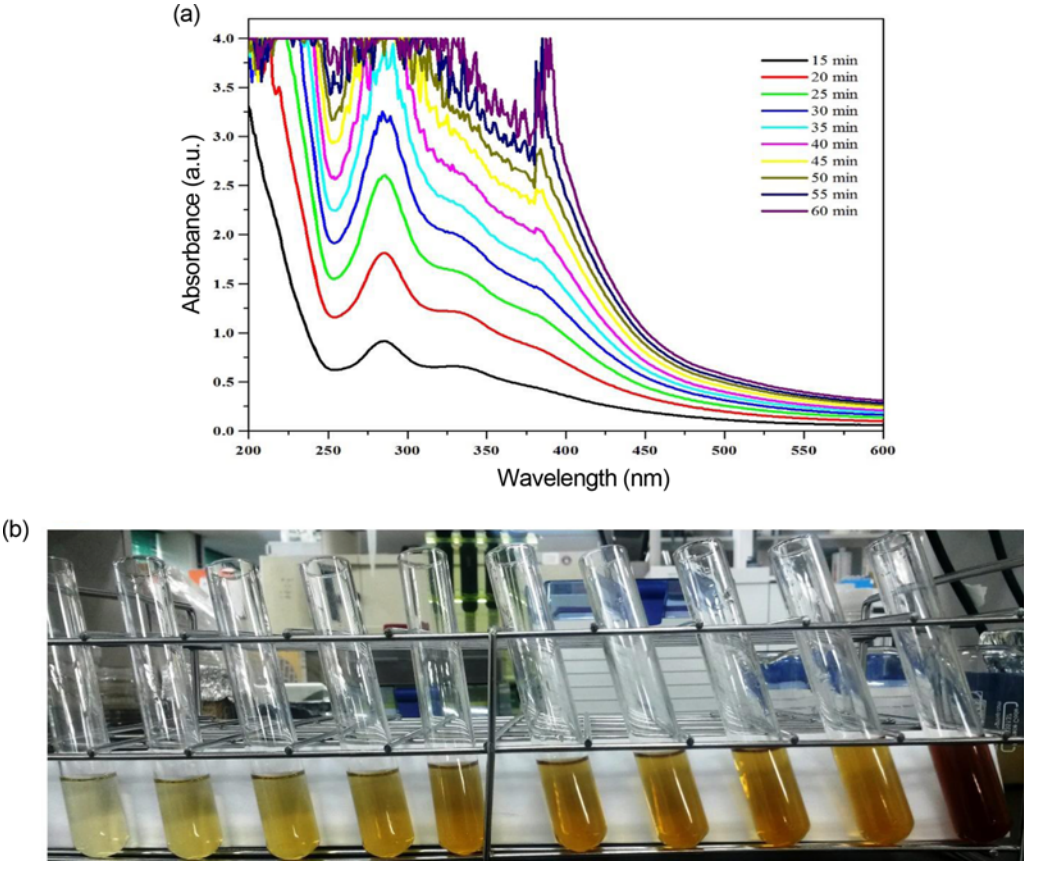
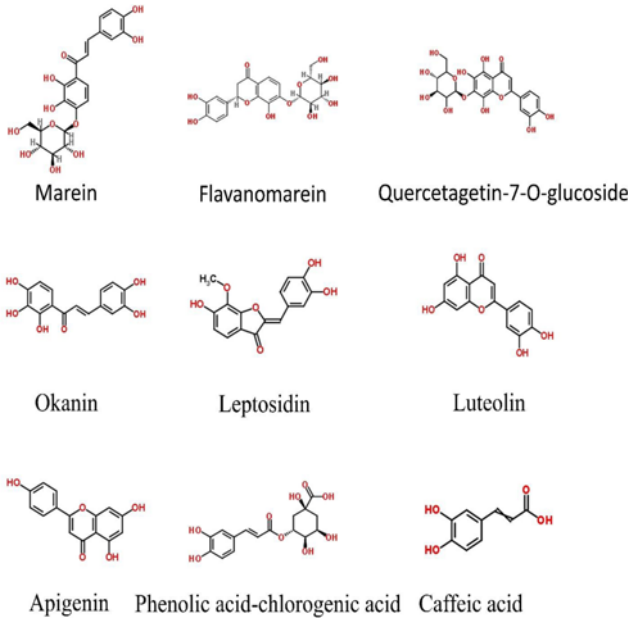


Figure 2. (a) UV-Vis spectrum for *C. tinctoria* brown dye extraction at different times and scanned wavelength from 200-800 nm, and (b) visual appearance of the dye at different extraction times.



Scheme 2. Chemical composition of *C. tinctoria* flower extract (Zalaru *et al*. 2014).

extraction of natural dye from plant sources and in the dyeing of textile materials. It is cost effective and reduces the time, chemicals, and energy required, as well as reducing effluent [1,24,25,35,36]. Zalaru *et al.* [37] extracted polyphenols and flavonoids from *C. tinctoria* Nutt. fruits extract using ultrasound and their chemical structures. The structures of polyphenols, acids, and flavonoids from *C. tinctoria* Nutt. fruits were shown in Scheme 2.

Effect of Time in *C. tinctoria* Dye Extraction Using Ultrasound

Our results indicate that there is a 10-fold increase in *C. tinctoria* dye extraction at the 60 min time point for both colors (yellow and brown) of dye using ultrasound and the conditions of 100 W and 80 °C, as shown in Figures 1(a), 1(b), 2(a) and 2(b). These results indicate that the rate of extraction increases after 25 min and subsequently remains high with a marginal increase for the 1 h process time.

Dyeing Optimization

Effect of Ultrasonic Power and Magnetic Stirring (rpm)

Overall dyeing optimization parameters like ultrasonic power, time, dye bath pH and temperature results are presented in Figures 3(a), (b), (c) and (d).

In order to identify the optimum conditions for leather dyeing with *C. tinctoria* dye, ultrasound conditions using different power and different rpm of magnetic stirring were studied and the results are presented in Figure 3(a). The dye concentration in the dye bath was monitored and is related to the amount of dye intake by the leather sample. It was found that the intake of both colors of *C. tinctoria* dye in leather

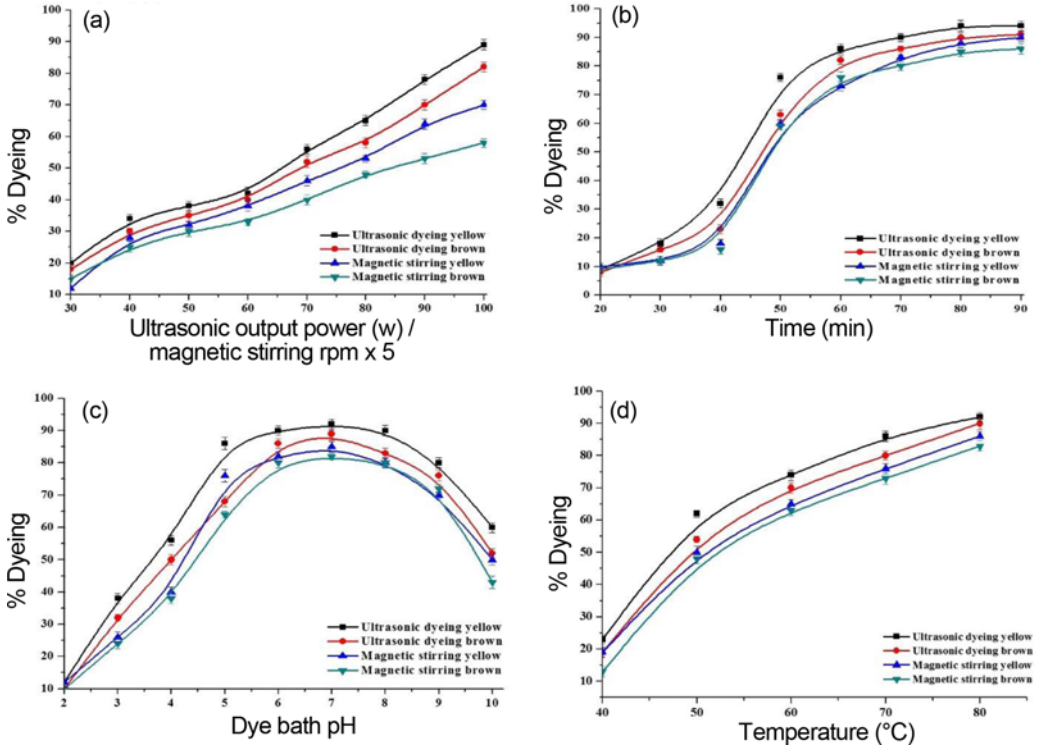


Figure 3. Percentage of dye bath exhaustion during leather dyeing with *C. tinctoria* yellow and brown dyes using various parameters: (a) ultrasonic power and rpm, (b) time, (c) pH and (d) temperature.

was greater in the case of ultrasonic dyeing (30-100 W) as compared to magnetic stirring (100-1000 rpm) over the course of the dyeing process, as shown in Figure 3(a). The increment of color strength due to US waves can be attributed by breaking up of low and high molecular weight aggregates into uniform dispersions in the dye bath and by releasing the gas or air molecules from leather into liquid to make cavitation. Therefore, the US waves will facilitate dye-leather contact and accelerate the rate of dye diffusion by piercing the insulating layer of leather. These results are consistent with those of Sivakumar *et al.* [1], who reported on the dyeing of leather with beet dye by ultrasound and magnetic stirring. Hence, natural dyeing of leather with ultrasound has been shown to be beneficial with an improved rate of exhaustion. Magnetic stirring is less beneficial in the natural dyeing of leather. The color strength of the dyed leather seemed to be directly proportional to the supplied power. The dye exhaustion percentages of the yellow and brown dye were found to be 78 % and 89 % in the ultrasonic assisted dyeing and 65 % and 52 % in the magnetic stirred dyeing, respectively Figure 3(a). Maximum dye uptake by leather during ultrasonic treatment can result from the uniform dispersion of dye into the dye bath and more breaches were developed in the leather matrix might be a cause. Consequently, the dye molecules may facilitate a leather-dye interaction and the dye will diffuse smoothly in leather. Perhaps, power ultrasound promotes the de-aggregation of dye molecules in the dye bath resulted in higher dye-uptake. However, a moderate level of dye uptake was observed when magnetic stirring was used Figure 3(a).

Effect of Time on Leather Dyeing by C. tinctoria Dye

The effect of dye fixation in the leather, evaluated using the percentage exhaustion of dye at different time intervals, is shown in Figure 3(b). It is evident from the figure that the uptake of dye increased gradually with time. It requires a maximum of 1 h to cause significant exhaustion of the dye bath. The dye uptake increased gradually from 20 min to 60 min and reached 86 % of yellow dye uptake by US, 82 % for brown dye uptake by US and 70 % of yellow dye uptake by MS and 73 % of brown dye uptake by MS at 1 h of dyeing time. Hence, 60 min of dyeing time with 100 W US power and 1000 rpm of MS have been demonstrated to be the optimum dyeing conditions. We observed no decline or incline in the peaks during the dyeing time; hence, we believe there was no desorption of the dye in the longer dyeing times.

Effect of pH on Leather Dyeing by C. tinctoria Dye

Figure 3(c) shows the results obtained with respect to the effect of pH on the exhaustion of dye in the process liquor. In this figure, it can be seen that the exhaustion of dye increased gradually as pH increases up to 7.0. Additional increases in pH resulted in a decrease in the exhaustion of dye, both in US and MS. Hence, we believe there will be desorption of the dye in the longer dyeing times at pH 8, 9 and 10. Maximum exhaustion of dye was observed with US treatment at pH 6.0 and 7.0 up to 92 % yellow, 89 % brown, and moderate yellow and brown dye uptake was observed by MS treatment up to 85 % and 82 %, respectively. Ultrasonic waves open up the fiber structure, and consequently, the diffusion of dyes into the leather matrix is higher at the optimized pH and results in maximum uptake. The effect of the dye bath pH can be attributed to the correlation between dye structure and crust leather. Since the *C. tinctoria* is a water-soluble dye, it reacts with the carboxyl groups of the

Figure 4. Leather dyed with *C. tinctoria* yellow and brown dyes. Left: control, with ultrasound yellow and brown; right: with magnetic stirring yellow and brown.

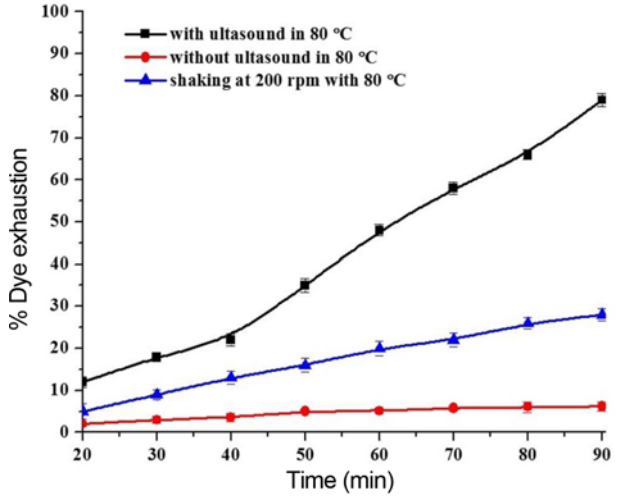


Figure 5. Influence of US, without US (still) and shaking at 200 rpm in a constant temperature at 80 °C on leather dyeing.

collagen and ionic molecules to form a chemical bridge between dye and leather to leave free from coordination at basic pH levels. This might be responsible for higher color strength and fastness properties. The pH 8, 9 and 10 shows a decline in the peaks during the dyeing time; hence, we believe there will be desorption of the dye in the longer dyeing times.

Effect of Temperature on Leather Dyeing by C. tinctoria Dye

As shown in Figure 3(d), the color strength of the dyed leather increased as the temperature was increased up to 80 °C. Indeed, heating increases leather swelling, and the breakdown of dye molecule aggregates in the solution increased. Thus, the diffusion of the dye molecules to the leather became easier and the dye exhaustion percentages increased in both the US and MS method, up to 92 %, 90 %, 86 %, and 83 % for the yellow and brown dyes, respectively. Above 40 °C, the dyeing percentage decreased slowly until it reached 50 °C, and then noticeably increased. The increase in exhaustion of dye could have been augmented with the distribution of dye aiding access to more reactive sites for interaction, as the dye molecules used are highly active at a temperature of 80 °C. Figure 4 shows the optimized dyeing condition we established with respect to ultrasound power (100 W), MS (1000 rpm), pH 7.0, time 60 min, and temperature 80 °C. Figure 5 shows the conditions of dyeing with US, without US and direct shaking with 80 °C, respectively. The results indicate US with 80 °C is efficient in leather dyeing compared to without US at 80 °C and shaking at 200 rpm with 80 °C.

Color Coordinates of Dyed Leather

Quantification of the color value of leathers dyed with natural *C. tinctoria* yellow and brown dyes obtained from both the US and MS methods was performed using reflectance measurements; the results were tabulated and are shown in Table 1.

The color values of the samples (L^*, a^*, b^*, c, h), with differences ΔL and Δa, are consistent with earlier reports on the natural dyeing of leather [2,29,38,39]. There was a significant improvement in the color intensity of the dyed leather and yellow color (corresponding to *C. tinctoria* dye) as inferred from the ΔL and Δa values when *C. tinctoria* extract was used with the US method, as compared to the MS method. Photographs of the dyed leather from the two experiments with the two colored dyes are shown in Figure 4.

To confirm the potential of US dyeing, three different types of leather dyeing (US, without US (still) and shaking at 200 rpm) were employed with a fixed dyebath temperature of 80 °C. The dye exhaustion values from each of these

Table 1. Ultrasonic and magnetic stirring dyeing of leather with *C. tinctoria* yellow and brown dye

S. no	Dyeing method	L^*	a^*	b^*	c	h	ΔL	Δa
1.	Control leather	22.3	1.3	1.6	4.9	189.0	-	-
2.	Ultrasonic dyeing of leather with yellow dye	-10.3	5.18	96.4	6.3	320.0	16.8	6.8
3.	Ultrasonic dyeing of leather with brown dye	-9.8	6.20	95.2	5.3	298.3	14.2	5.3
4.	Magnetic stirring of leather with yellow dye	-9.2	5.94	95.3	4.1	321.0	11.6	5.6
5.	Magnetic stirring of leather with brown dye	-9.2	6.68	96.1	4.8	330.6	12.2	6.9

Table 2. Organoleptic properties and visual assessment data of control and dyed leathers at optimized conditions (rating average values)

S. no	Dyeing method	Fullness	Grain smoothness	Softness	Grain tightness	Uniformity	General appearance
1.	Control leather	6.4	6.2	6.0	6.9	6.2	6.1
2.	Ultrasonic dyeing of leather with yellow dye	6.8	6.9	6.4	7.2	6.9	6.7
3.	Ultrasonic dyeing of leather with brown dye	6.7	6.8	6.6	7.0	6.24	6.7
4.	Magnetic stirring of leather with yellow dye	6.5	6.8	6.4	7.6	6.9	6.8
5.	Magnetic stirring of leather with brown dye	6.5	6.6	6.4	7.2	6.8	6.9

methods are presented in Figure 5. US mediated leather dyeing resulted in 79 % dye exhaustion, followed by shaking at 200 rpm, and the very least dye exhaustion was observed with still dyeing.

Organoleptic Properties and Visual Assessment of Dyed Leathers

The organoleptic properties were evaluated and a visual assessment for fullness, grain smoothness, softness, grain tightness, uniformity and general appearance of the control and experimental leathers (optimized dyeing conditions) was carried out using a standard tactile evaluation technique. The determined values are detailed in Table 2.

The fullness, grain smoothness, softness, grain tightness, uniformity and general appearance was uniform for leathers dyed using US and MS with yellow and brown colors; this finding is in agreement with the reflectance measurement values. The intensity of the dyed leather was comparatively higher than the control. There was no appreciable change or shift in color for the experimental leathers compared to the control. These results are in agreement with the reflectance measurement values. There was an overall improvement in the general appearance of the leathers dyed with *C. tinctoria* dye. The results demonstrate that all the organoleptic properties are comparable with those of chemically dyed leather samples. The uniformity of color, dye penetration and shade were moderate for the pigment dyed leather samples.

Fastness Properties of Dyed Leather

The results of our evaluation of the fastness properties indicated that the dry fastness values for both US and MS *C. tinctoria* dyes were excellent and were found to be comparable. However, the values for wet rub and perspiration resistance were poor, a finding which was not unexpected. The reason for this is likely due to the fact that no mordant was employed during the natural leather dyeing process. It is a generally accepted practice to use conventional metal mordents in dyeing with natural materials. Since the application tested here relates to health sensitivities, metal mordents may pose a toxicity risk, which would be an undesirable result. Hence, research on suitable eco-friendly alternative mordents is being pursued in our laboratory in order to improve the wet rub and perspiration resistance.

Conclusion

C. tinctoria flower petal dye consists of two shades of dye: yellow and brown. In our study, the dye was extracted with the help of US, and leather was dyed with the extracted colors as an eco-friendly method. The leather dyed with *C. tinctoria* dyes using our optimized conditions resulted in the uniform dyeing of leather with an intense bright shade. The overall fastness of the *C. tinctoria* color extract dyed leathers was comparable with those obtained with control leathers. The strength characteristics of the control leathers were not significantly altered. The bulk properties of the leather, like fullness, grain smoothness, softness, grain tightness, uniformity and general appearance, were improved by the *C. tinctoria* dye in the process bath. Since the process involves natural material of a non-toxic and nutritious nature, it is highly suitable for the dyeing of fibrous substances, such as leather, and for use in health sensitive applications. The present approach will provide a new avenue for the development of environmentally friendly natural dye extraction and leather dyeing processes.

Acknowledgements

This research was supported by grant number 315033-3, iPET (Korea Institute of Planning and Evaluation for Technology in Food, Agriculture, Forestry and Fisheries). This research was supported by grant number 313058-1, iPET (Korea Institute of Planning and Evaluation for Technology in Food, Agriculture, Forestry and Fisheries).

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