

VALEKS VE KINA KULLANIMI VE MÜTEAKİP MORDANLAMININ DERİDE SERBEST FORMALDEHİT VE CR(VI) OLUŞUMU ÜZERİNE ETKİSİ

THE EFFECT OF VALONEA AND HENNA TREATMENT AND POST-MORDANTING ON CR (VI) AND FREE FORMALDEHYDE FORMATION IN LEATHER

Hasan ÖZGÜNAY,¹ Onur YILMAZ,^{1*} Urana DANDAR,¹ Selime ÇOLAK,¹ Gökhan ZENGİN,¹ Altan AFŞAR,¹ Demetra SIMION,² Carmen GAIDĂU²

¹Leather Engineering Department, Faculty of Engineering, Ege University, İzmir
²INCDTP- Division ICPI, 93 Ion Minulescu st., sector 3, Bucharest, Romania

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ABSTRACT

Present study aims the use of natural vegetable tannins as antioxidant phenolic materials in the processing of chromium tanned leathers and to investigate their effect on Cr(VI) and free formaldehyde formation. For this purpose valonea and henna were selected as tannins and their antioxidant capacities were determined by FRAP and TEAC/ABTS methods. These vegetable tannins were used in retanning process of chromium leathers in combination with copper, aluminium and iron based mordants to evaluate their potential on reduction of Cr(VI) and formaldehyde content of the leathers as well as their effect on colour tones.

Keywords: Antioxidant effect, Leather, Chromium (VI), Formaldehyde, Mordanting

ÖZET

Bu çalışmada krom tabaklanmış derilerin üretiminde antioksidan fenolik materyaller olarak doğal bitkisel tanenlerin kullanımı ve bunların deride Cr(VI) ve formaldehit oluşumu üzerine etkilerinin araştırılması hedeflenmiştir. Bu amaçla tanen olarak valeks ve kına seçilmiş ve bunların antioksidan kapasiteleri FRAP ve TEAC/ABTS yöntemleri kullanılarak belirlenmiştir. Bu tanenler krom tabaklanmış derilerin retenaj işleminde bakır, alüminyum ve demir esaslı mordanlarla birlikte kullanılarak derilerin Cr(VI) ve formaldehit içeriklerinin düşürülmesine yönelik potansiyelleri ve renk tonları üzerine etkileri değerlendirilmiştir.

Anahtar Kelimeler: Antioksidan etki, Deri, Krom (VI), Formaldehit, Mordanlama

Corresponding Author: Onur Yılmaz, e-mail: onur.yilmaz@ege.edu.tr

1. INTRODUCTION

In the last decades the increasing concern about the potential health hazards of toxic chemicals in consumer articles such as leather products forced many countries producing or importing these articles to introduce stringent stipulation for the permissible levels of such chemicals in the products (1,2). Regarding the leather articles the most important technical issues concerning ecology and consumer health are the formation of chromium (VI) and free formaldehyde in the final products (3).

Since 1858 F.Knapp raised the basic theory of chrome tanning, the application of more than one hundred years of history has proved that chrome tanning method has a number of superior performances which can't be replaced with other inorganic or organic tanning materials. Thus, in leather production the chrome tanning method has been the

most widely used tanning system since then all over the world (4,5). Normally chrome tanning merely involves Cr(III), however, there have been many reports mentioned about abnormally detection of Cr(VI) in some leather samples (6-8). Chromium in its +3 state has the highest stability to oxidation and is considered to play an important role in glucose (9,10), lipid and protein metabolism, therefore it's assumed as nontoxic. However, chromium in its +6 state is highly toxic (11), mutagenic and carcinogenic to humanity and animals causing damage to skin, mucous membrane and respiratory tract (12). Dermal contact with Cr(VI) compounds can cause allergic dermatitis, while this effect has not been generally observed for Cr(III) compounds (1,13,14). The exact origin of Cr(VI) in leather is not well understood. However, pigments based on lead chromate (7,15), the incompletely reduced chromium tanning agents and metal complex dyes containing Cr(VI) are known to be

the primary sources of hexavalent chromium, which can be easily avoided in the processes. However, the most difficult aspect of the problem is the possibility of oxidative conversion of unbounded Cr(III) to Cr(VI) during the manufacture (16,17) or during the use of products. Fatliquors based on oils with a high degree of unsaturation, other post-tanning and finishing auxiliaries used in the processing of leather bearing uncured or excess of oxidative catalysts could, theoretically, aid in the conversion of free Cr(III) to Cr(VI) (18,19). The hydroperoxide formed during auto-oxidation of the fat/oil (20,21), oxidizes Cr(III) to Cr(VI) in chrome-tanned leather. Various other auxiliaries such as acrylic resins and binders used in the post-tanning and finishing operations, respectively, may also contribute to the formation of Cr(VI) due to the presence of residual oxidative catalysts used in their manufacture (1). Many studies related with Cr(VI) in leather have been conducted recently to understand the release of Cr(VI) and Cr(III) (22), to reduce or avoid the use of chromium tannage in leather manufacturing (23-26) as well as to reduce chromium containing waste-waters (27). Recently Denmark did propose to limit the amount of Cr(VI) in leather by Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (28). A restriction has been decided and it is anticipated to enter into force within the European Union (EU) in 2015 (29). The permissible limit of Cr(VI) is 3 mg/kg_{leather} according to the ISO 17075 standard (19) for leather products. Therefore, the elimination of Cr(VI) formation in leather products has gained a crucial importance in the last years.

Along with Cr(VI), free formaldehyde release constitutes another important issue for leather industry (3). In spite of the fact that formaldehyde is a naturally occurring substance, which is produced and used in every living cell of plants, animals and humans at very low concentrations, at the high concentrations that can occur in the chemical industry and laboratories, it is an irritating, reactive, toxic and flammable chemical that should be handled with due care in a professional way (30). Owing to its toxic effects, direct use of formaldehyde in leather processing is forbidden; however, there is always a risk of formaldehyde formation in leathers due to other sources. Formaldehyde is used as a condensation agent in the production of chemicals such as syntans, resin tanning agents and dyeing auxiliaries which can be the main sources of the problems associated with formaldehyde (31-33). These condensation products show varying stability to hydrolytic reactions that can lead to the release of formaldehyde. Moreover, the synergistic effects through the interactions of these chemicals with the leather matrix and the ageing of unsaturated organic substances (e.g. fatliquors) also may cause aldehyde formation in the products (34).

The chemicals used in manufacturing and environmental factors that the product is exposed during its use such as heat, light, humidity, etc. may cause ageing and structural deformations in the product. These structural changes may include the oxidation of Cr (III) to Cr (VI), decrease in shrinkage temperature, fading or yellowing, loss of physical resistance, odour problems due to oxidation of fatliquors and formaldehyde release. These deformations generally occur due to the oxidant groups which are called as free radicals that arise depending on the factors mentioned above.

Hindering the formation of free radicals usually prevents the occurrence of Cr(VI) and formaldehyde in the products. Antioxidants are well known to be effective for the elimination of free radicals. As it's acknowledged in the food and medicine sectors, vegetable extracts (tannins) have a great antioxidant activity (35). Tannins which possess multiple phenolic hydroxyl groups have been shown to be strong inhibitors of Cr(III) oxidation into Cr(VI) (36). Retanning process using vegetable tannins like quebracho and sumac extracts has been demonstrated to be efficient against Cr(VI) formation in leathers exposed to light (37). The application of a vegetable retannage whenever possible seems to be a solution against formation of Cr(VI) in leather.

Synthetic dyestuffs are widely used in leather industry for colouring of leathers. Acid dyes and metal complex dyes are the most important and widely used dye groups for this purpose (38). At the end of the dyeing process the remaining floats are discharged to wastewaters which usually contain unreacted dyestuffs. The high degree of organics and/or heavy metals present in these remaining dyes that pass into wastewaters are difficult to remove by conventional physicochemical and biological treatment methods (39). Many dyes used in leather treatment and emitted into environment can biologically transform to toxic species and cause interference in natural photosynthetic processes (40,41). The solution for the problem caused by synthetic dyestuff might be to reduce their discharge into float and/or to replace them with natural dyes. Recently, there is a great interest on the leather products with natural look and/or processed in an ecological manner. From this point of view, the individual colour properties of vegetable tannins and the colours they offer to resultant leathers have great importance (42), and they provide opportunity to be used as natural colouring materials beside their tanning properties.

In the present study, henna (*Lawsonia Inermis*) which have been extensively used for centuries in the Middle East, Far East and Northern Africa as dye for nails, hands, hair and textile (43), and valonea as a well-known vegetable tannin were used in leather production as retanning and/or natural colouring materials. Prior to their use the antioxidant powers of both tannins were determined and their efficiency on the prevention of Cr(VI) and formaldehyde formation was investigated. The colour of the leathers processed with henna and valonea as natural colouring materials was also evaluated and their colour tones were varied by using three types of mordants based on aluminium, copper and iron. The effects of the mordants on colour tones of the leathers as well as on the formation of Cr(VI) and formaldehyde was reported. Present study shows a route for the production of ecological leather articles lowering the risk of Cr(VI) and formaldehyde formation and eliminating the use of synthetic dyes.

2. MATERIAL AND METHOD

2.1 Materials

As natural vegetable materials commercial valonea tannin (in extracted form) (Artu Kimya) and henna powder (in grinded form) were used in the research. The leather material used in the study was a wet-blue leather which was obtained from 15-20 kg calfskin and processed conventionally in a regional tannery (Sepiciler Co.) The

leather was shaved to 1.25 mm thickness and the coupon area of the leather was cut into pieces in size of 15x21 cm prior to experiments.

In the analysis, analytical grade sodium acetate trihydrate (Merck), glacial acetic acid (Merck), hydrochloric acid (Merck), TPTZ [2,4,6 tris (2-*pridyl*-s-triazine)] (Sigma), iron (III) chloride (FeCl₃.6H₂O) (Merck), ABTS [2,2-azinobis (3-ethylbenzothiazoline-6-sulphonic acid) ammonium salt] (Sigma), trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) (Sigma), potassium peroxodisulphate (J.T.Baker), dipotassium hydrogen phosphate (Merck), phosphoric acid (Merck), 1,5-diphenylcarbazide (CO(NHNHC₆H₅)₂) (Merck), acetone and methanol (Merck), aluminium (KAl(SO₄).18H₂O) (Horasan Chem.), iron (FeSO₄.7H₂O) (Merck) and copper (CuSO₄.5H₂O) (Uprac Chem) were used.

2.2. Method

2.2.1. Determination of Antioxidant Powers of Valonea and Henna

Antioxidant properties of vegetable materials were measured by FRAP (Iron (III) Reducing Antioxidant Power) and TEAC/ABTS (Trolox Equivalent Antioxidant Capacity) methods (44). For the analysis, 0.1 g of henna was extracted in 25 mL of methanol for 24 h. 0.1 g of valonea was dissolved in 25 mL of water:acetone mixture (1:1) before the analysis. Both solutions were diluted appropriately and their antioxidant powers were calculated according to trolox equivalents.

The FRAP method measures antioxidant power by using the ferric reducing ability of plasma; the ferric tripyridyltriazine (Fe(III)-TPTZ) complex to ferrous tripyridyltriazine (Fe(II)-TPTZ) by a reductant at low pH. Fe(II)-TPTZ has an intensive blue colour and can be monitored at 593 nm. In the analysis; TPTZ, 10x10⁻³ M was prepared in 40x10⁻³ M HCl. 20x10⁻³ M FeCl₃ was prepared by dissolving FeCl₃.6H₂O. TPTZ and ferric chloride solutions were diluted in 300 mM sodium acetate buffer (pH 3.6) at a ratio of 1:1:10. Standards or extracts (both 150 µL) were added to 2850 µL of the FRAP solution and the absorbance was determined after assay samples were allowed to react for 30 min.

The trolox equivalent antioxidant capacity method (TEAC/ABTS) is based on inhibition of chromogen radical cation's absorbance by hydrogen donating antioxidants. By using reduction in absorbance the total antioxidant capacity can be determined as trolox equivalent. Antioxidant ranking was established based on their reactivity relative to a 1.0 mmol/L trolox standard. In analysis; trolox, 1x10⁻³ M was prepared in 96% ethanol. The chromogenic radical reagent ABTS⁺, at 7x10⁻³ M concentration was prepared by dissolving 2.45x10⁻³ M potassium persulfate. The resulting ABTS radical cation solution was left to mature at room

temperature in the dark for 12–16 h and was diluted 90 times with acetate buffer (pH= 4.5) and was named as working solution throughout the work for TEAC (Trolox-equivalent antioxidant capacity assays). 50µL trolox (varied between 0 and 2x10⁻³ M) or extract solutions were added to 2950 µL of the working solution and the absorbance at 734 nm were read at the end of 10 min. Both of the analyses were done in duplicates and the results are given as mean values.

2.2.2. Use of Valonea/Henna in Leather Processing

Prior to the use of valonea and henna in leather processing their tannin contents were investigated according to related standards (45-48) and the results are given in Table 1.

Previously chromium tanned and shaved leathers were processed according to the receipt given at Table 2 in laboratory scale re-tanning drums with temperature control. Additionally, two control samples were processed under the same conditions except using any vegetable tannin. The commercial henna used in the study was not in an extracted form. Therefore, to establish the amount of henna to be used in leather processing, henna powder was extracted at 50 °C (at fatliquoring temperature) for 4h and the extractable solid amount was determined gravimetrically as being 25 wt%. As ¼ amount of the unextracted henna would pass into the float, 4, 10, and 20 wt% (based on wet-blue weight) of henna ratios were chosen to be used in the trials. The valonea was a commercial product in extracted form; therefore it was used in the ratios of 1, 2.5 and 5 wt% equivalent to the henna extract. Additionally, the leather samples retanned with vegetable materials were treated with 1 wt% of aluminium, iron and copper mordants to vary the shade of natural colours of the leathers.

Before the characterizations, the processed leathers were dried at room temperature for few days and reconditioned at certain temperature and humidity.

2.2.3. Artificial Ageing of Leather Samples and Determination of Cr(VI) and Formaldehyde Contents

Cr(VI) and formaldehyde contents of the leather samples were determined according to ISO 17075 (19) and ISO 17226-1(49) standard test methods. In many studies it was stated that the formation of Cr(VI) was triggered or increased by certain factors e.g. high pH values, temperature and UV light, etc (50). Exposing the leathers to UV light, initially which do not contain Cr(VI) may cause gradual occurrence of this element as shown by Font et al. (51) and Candar et al.(52) Therefore, to stimulate the formation of Cr(VI) the leather specimens were exposed to UV light (360 nm) at 80°C for 7 days (53). The chromium VI and formaldehyde contents of the leathers were re-measured after accelerated ageing process. All of the analyses were done in duplicates and the results are given as mean values.

Table 1. Tannin analysis results of valonea and henna

Vegetable Material	Insoluble matters (%)	Soluble matters (%)	Tannins (%)	Nontanins (%)
Henna	42.07	57.93	16.44	41.49
Valonea	6.03	93.97	68.83	25.14

Table 2. The recipe used for the processing of chromium tanned leathers

Process	%	Product	°C	Min	Notes
Washing	200	Water	35		
	0.2	HCOOH		30	
Neutralization	150	Water	35		
	2.5	Neutralising syntan		15	
	0.5	NaHCO ₃		45	pH:5-5.5
Washing	200	Water	35	20	
Retanning	150	Water	40		
	x	Vegetable material (Valonea / Henna)		15	
	2	Condensed naphtalene sulphone acid		15	
	3	Phenol sulphone condensation product		15	
	3	Melamine-Urea formaldehyde resin		15	
Fatliquoring	5	Sulphited mix of natural fatliquors	45		Float heated
	2	Synthetic fatliquor-I			
	2	Synthetic fatliquor-II		45	
	1	HCOOH		30	
	0.5	HCOOH		30	pH: 3.8
Washing	1	Mordant		60	
	200	Water	35	20	

2.2.4. Determination of the Colours of Leather Samples

Minolta CM-508d spherical spectrophotometer (Minolta Co. Ltd. Japan) with 8 mm diameter of measurement area was used for measuring the colours of leather samples. Spectral reflectance values were measured between 400-700 nm range with 20 nm intervals, and 16 readings were obtained for each sample. The measurements were done under the conditions of CIE 10° standard observer angle and CIE standard D65 light source. The reflectance readings were converted to CIE L*a*b* values by using related formulas, and colour differences were calculated by CIELAB 1976 colour difference formula (54).

3. RESULTS AND DISCUSSION

3.1. Antioxidant Powers of Valonea and Henna

Considering the results obtained by FRAP and TEAC/ABTS methods; it was clearly seen that antioxidant power of valonea was considerably higher than henna (Table 3). At this point it is necessary to mention that the valonea sample used in the analysis was in extracted form while the henna sample was not extracted product.

3.2. Cr(VI) and Formaldehyde Contents of Leather Samples

The Cr(VI) and formaldehyde contents of the processed leathers are given in Table 4. The analyses were performed in duplicates for each specimen and average values were presented. Prior to the ageing process, no Cr(VI) was detected neither in blank nor in valonea or henna treated leather samples. After artificial ageing process 23.6 and 35.5 ppm Cr(VI) values were detected in blank samples which did not contain any vegetable tannins in the process.

That means an important amount of Cr(III) was oxidized to Cr(VI) under the drastic conditions applied to the specimens (Table 4).

Considering the valonea treated leather samples; the increasing amount of valonea used in retanning resulted in significantly reduced values of Cr(VI) in aged leathers verifying the efficiency of valonea tannin on the prevention of Cr(VI) formation. For instance, the Cr(VI) content of 1 wt% valonea treated aged leathers was found to be 6.6 ppm as being much lower than the level of blank specimens. When the ratio of valonea was increased to 5 wt% the Cr(VI) content was decreased significantly to 0.65 ppm for the aged leathers. In the case of henna treated leathers, the content of Cr(VI) was also decreased remarkably, however, the reduction ratios were lower than the values obtained with valonea. The use of 4 wt% henna in retanning resulted in almost 50 % decrease in Cr(VI) content of the blank specimens, whereas the increased use of henna (20 wt%) led to a decrease of 67-77% in Cr(VI) levels of the leathers. It was observed that the ability of both tannins on the prevention of Cr(VI) formation was in accordance with their antioxidant powers since the valonea had much higher antioxidant power than henna.

In the experiments, the effect of three mordant types (Al, Cu and Fe) on Cr(VI) formation was also evaluated. From the results it was obvious that all mordant types had positive effect on the formation of Cr(VI) and lower values were observed in comparison to valonea/henna treated leathers. Among the mordants, iron was found to be more effective than aluminium for the formation of Cr(VI), however, the best results were obtained with copper treated leathers where the Cr(VI) levels were decreased below or near the detection limits (< 3ppm) for all aged leathers.

Table 3. Antioxidant powers of henna and valonea determined by FRAP and TEAC/ABTS methods

Vegetable Material	Antioxidant powers (FRAP-mmol/L)	Antioxidant powers (TEAC/ABTS – mmol/L)
Henna	2.3	2.4
Valonea	48.1	28.0

Table 4. Cr(VI) and formaldehyde contents of leather samples before and after ageing

Sample	Before aging Cr(VI) (ppm)	After aging Cr(VI) (ppm)	Before aging Formaldehyde (ppm)	After aging Formaldehyde (ppm)
Blank 1	n.d.	23.60	22.60	19.40
Blank 2	..	35.50	18.45	18.70
1% Valonea	..	6.60	13.85	9.55
1% Val + 1 % Al	..	5.15	12.25	7.95
1% Val + 1 % Cu	..	n.d.	11.65	7.30
1% Val + 1 % Fe	..	2.50	13.15	11.80
2.5% Valonea	..	2.70	19.90	7.90
2.5% Val + 1 % Al	..	2.05	15.45	6.50
2.5% Val + 1 % Cu	..	n.d.	17.25	9.20
2.5% Val + 1 % Fe	..	0.80	15.10	9.35
5% Valonea	..	0.65	13.55	5.05
5% Val + 1 % Al	..	0.70	13.80	6.10
5% Val + 1 % Cu	..	n.d.	9.90	5.40
5% Val + 1 % Fe	..	0.75	8.90	7.85
4% Henna	..	13.35	15.45	9.50
4% Hen + 1 % Al	..	13.50	15.40	8.50
4% Hen + 1 % Cu	..	0.30	18.60	10.10
4% Hen + 1 % Fe	..	5.10	18.60	11.00
10% Henna	..	12.00	14.35	10.10
10% Hen + 1 % Al	..	10.10	11.90	6.60
10% Hen + 1 % Cu	..	0.15	11.90	7.20
10% Hen + 1 % Fe	..	2.75	12.80	7.30
20% Henna	..	7.90	16.35	11.65
20% Hen + 1 % Al	..	8.25	10.05	9.85
20% Hen + 1 % Cu	..	0.20	12.20	10.10
20% Hen + 1 % Fe	..	2.75	14.50	12.25

n.d. : not detectable

It is difficult to explain the behaviour of copper's extraordinary Cr(VI) formation preventing performance due to the complex structure of leather matrix containing other substances i.e. tanning/retanning, fatliquoring agents, etc. Moreover, it's also known that complexation reactions vary the oxidation and reduction potentials of ions which affect their antioxidant behaviours. So, here it can be attributed to the higher oxidation capacity of copper complex that reacted more efficiently with free radicals occurred during the ageing process.

Before the aging process, the measured formaldehyde content of the blank leathers was found to be 18.4 and 22.6 ppm which was not surprising since the selected synthetic tannins had potential to cause free formaldehyde formation due to their structures. However, noticeable decrease in formaldehyde levels was observed for both valonea and henna retanned leathers where the free formaldehyde levels were in the range of 13.8 – 19.9 ppm. Nevertheless, no realistic correlation was found between the increasing ratio of tannins and the decrease ratio of free formaldehyde values. As comparison of the efficiency of both tannins, the valonea seemed to be slightly more effective in avoiding free formaldehyde formation. On the contrary to the Cr(VI) results, the ageing process had a positive effect on free formaldehyde formation where a general decrease was observed for all samples after artificial ageing. Moreover, the valonea tanned leathers showed more than 50% decrease in free formaldehyde content of leathers after ageing process and best results were obtained with 5 wt% valonea treated leathers with 5 ppm. In addition, the use of

mordants did not have a remarkable effect on free formaldehyde formation in the leathers, however, a general decrease could be observed in formaldehyde contents regardless to the type of mordant used.

3.3. Colors of The Leather Samples Treated with Valonea/Henna

Considering the CIE L, a and b values obtained by colour measurements (Table 5); it was observed that b* values of the leather samples showed a proportional increase with the increasing amount of valonea which refers a shifting to yellow tones. The aluminium and copper mordants didn't have a significant effect on the colour of valonea retanned leathers. However, L and b* values of the samples were lower with the use of iron mordant. It was also observed that the colours went to darker and the shade of dominant yellow colour decreased in the case of iron mordant. In addition, the colour of these samples varied from lighter to dark anthracite depending on the ratio of valonea (Table 5).

For the samples treated with henna, an increase was also observed in b* values proportional to the amount of henna referring to an increase in the intensity of yellow colour shade. Similarly to the case of valonea, the aluminium and copper mordants didn't result in a noticeable change in colours of the leathers. However, in the case of iron mordant L and b* values were decreased where the colours showed a variation from light to dark green shades with the increase of henna ratios. With a comparison of the valonea and henna treated leathers in general, it can be said that the

colours of henna treated leathers had higher b values and accordingly darker yellow tones in comparison to the valonea retanned leathers (Table 5).

4. CONCLUSIONS

The artificial ageing process exhibited a significant influence on the formation Cr(VI) in the leathers. However, the Cr(VI) contents of the leathers were remarkable lowered with use of vegetable materials. Valonea was found to be more effective for the prevention of Cr(VI) formation than henna which was in accordance with their antioxidant capacity determined by both FRAP and TEAC/ABTS methods. Moreover, the use of mordants had also significant effect on the reduction of Cr(VI) values where copper mordant resulted in Cr(VI) values below or near detection limits. Vegetable retanned leathers also showed lower free formaldehyde contents in comparison to the control samples. Valonea was slightly more efficient than henna in prevention of free formaldehyde and showed more than 50% reduction in formaldehyde contents of the leathers. Consequently, any ratio of vegetable tannin with copper mordanting for Cr(VI) formation prevention and 5% valonea














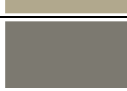












or 10% henna for decreasing formaldehyde release can be recommended.

The natural colour of the leathers treated with valonea or henna was relatively diversified by using three different inorganic mordant types. Depending on the mordant type different tones of yellow, anthracite and green were able to be obtained by mordanting process without using any synthetic dyes. Present study showed the possibility to produce leather articles in a more ecological manner by lowering and/or preventing the formation of toxic chemicals such as Cr(VI) and formaldehyde as well as by avoiding the use synthetic dyes. Moreover, although there are several reports regarding the preventing effect of vegetable materials on Cr(VI) formation in leathers, the superior effect of mordanting on Cr(VI) formation is reported for the first time by this study.

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Table 5. Colours of the leather samples treated with valonea/henna and with different mordants

Colour	Samples	L	a	b	Colour	Samples	L	a	b
	Blank 1	79.73	-2.94	4.61		Blank 2	81.84	-3.53	3.62
	1% Valonea	72.72	-1.67	11.25		4% Henna	75.34	-1.61	14.12
	1% Valonea + 1% Al	70.90	-0.79	12.36		4% Henna + 1% Al	75.06	-1.88	16.48
	1% Valonea + 1% Cu	70.20	-0.85	11.86		4% Henna + 1% Cu	70.30	-1.84	14.11
	1% Valonea + 1% Fe	55.78	-2.08	0.58		4% Henna + 1% Fe	63.34	-0.44	7.88
	2.5% Valonea	72.57	-1.28	13.14		10% Henna	70.21	-0.10	16.74
	2.5% Valonea + 1% Al	72.90	-0.84	15.55		10% Henna + 1% Al	70.20	-0.22	18.02
	2.5% Valonea + 1% Cu	67.70	0.11	15.37		10% Henna + 1% Cu	68.09	-0.38	16.45
	2.5% Valonea + 1% Fe	47.68	-1.35	-1.84		10% Henna + 1% Fe	50.81	0.02	6.07
	5% Valonea	72.94	-0.57	15.63		20% Henna	69.26	1.46	19.69
	5% Valonea + 1% Al	70.07	-0.91	14.94		20% Henna + 1% Al	66.36	1.43	22.89
	5% Valonea + 1% Cu	68.75	1.53	17.17		20% Henna + 1% Cu	61.62	0.34	20.48
	5% Valonea + 1% Fe	44.00	-1.09	-3.10		20% Henna + 1% Fe	44.34	0.11	7.05

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