

Reduction of Hexavalent Chromium Formation in Leather with Various Natural Products (*Coridothymus capitatus*, *Olea europaea*, *Corylus avellana*, and *Juglans regia*)

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Abstract

In this research, the extracts obtained from various natural products (hazelnut shells, thyme, olive shoots, and walnut leaves), which are indicated to have antioxidative characteristics, which are used during the retanning stage of leather manufacturing and their effects on chromium(VI) formation in leather was examined. Finished leathers were exposed to ageing conditions for 24h at 80°C and for 24h and 72h at 80°C under UV in order to enable chromium(VI) formation in the leathers. Chromium (VI) amounts in each leather sample were measured with a Shimadzu UV-1601 PC UV-Visible spectrophotometer at 540 nm according to the ISO/FDIS 17075 standard method, and how each extract affected chromium (VI) formation in leather was examined. According to the findings of the research; *Coridothymus capitatus*, *Olea europaea*, *Corylus avellana*, and *Juglans regia* extracts, which were used during the retanning stage of leather manufacturing, significantly reduced chromium(VI) formation in the leather under all three ageing conditions. The best reduction was obtained with *Coridothymus capitatus* extract in the ratio of 89.24% under the ageing condition of 24h/80°C. It is recommended that different extraction methods, different natural extracts, and different ageing conditions be carried out in the future are to optimize the results of the current study.

Keywords: Ageing, antioxidants, chromium(VI), leather, plant extract.

Çeşitli Doğal Ürünler ile Deride Hekzavalan Krom Oluşumunun Azaltılması (*Coridothymus capitatus*, *Olea europaea*, *Corylus avellana* ve *Juglans regia*)

Özet

Bu araştırmada, antioksidatif özelliğe sahip olduğu bilinen çeşitli bitkilerden elde edilen ekstraktlar deri işlentinin retenaj aşamasında kullanılarak deride krom(VI) oluşumuna etkileri incelenmiştir. Mamul hale gelen deriler 80°C sıcaklık'ta 24 saat, 80°C sıcaklık/UV altında ise 24 saat ve 72 saat yaşlandırma koşullarına maruz bırakılarak derilerde krom(VI) oluşumu sağlanmıştır. Her bir deri örneğinde krom(VI) miktarları Shimadzu UV-1601 PC UV-Visible spektrofotometre ile 540 nm'de ISO/FDIS 17075 standart metoduna göre ölçülmüş ve her bir ekstraktın deride krom(VI) oluşumunu ne şekilde etkilediği incelenmiştir. Araştırma sonuçlarına göre; deri işlentinin retenaj aşamasında kullanılan *Coridothymus capitatus*, *Olea europaea*, *Corylus avellana* ve *Juglans regia* ekstraktlarının üç yaşlandırma koşulunda da derideki krom(VI) oluşumunu önemli oranda azalttığı tespit edilmiştir. En iyi azalma %89,24 oranı ile 24 saat/80°C yaşlandırma koşulunda *Coridothymus capitatus* ekstraktı ile elde edilmiştir. Farklı ekstraksiyon yöntemleri, farklı doğal ekstraktlar ve farklı yaşlandırma koşulları elde edilen sonuçların optimizasyonu açısından ileride yapılacak yeni çalışmalar için önerilebilir.

Anahtar Kelimeler: Antioksidanlar, bitki ekstraktı, deri, krom(VI), yaşlanma.

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INTRODUCTION

In recent years, similar to that in all branches of industry, the interest in ecological products has also increased dramatically. In this context, the companies and researchers are conducting various studies related with ecological friendly leather production (Zengin et al. 2012). Natural products are included in various processes of leather

production. For example, various herbal products are used for antimicrobial affect, formaldehyde elimination, and for natural dyeing in the leather processes (Bayramoglu 2006, Bayramoglu et al. 2006, Bayramoglu 2007, Bayramoglu 2010, Bayramoglu et al. 2011, Onem et al. 2011).

The hexavalent chromium content in leather is the leading toxic chemical content that is highly

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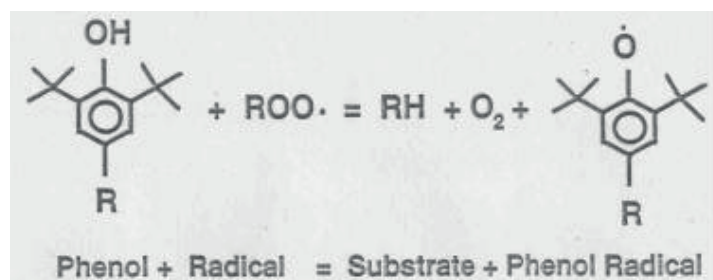


Fig. 1. Reaction with primary antioxidants (Puntener, 1996).

considered and requested for analysis during export of products as a regulatory requirement. For example, the major European retail group C&A issued a recall notice for two models of baby shoes after tests showed signs of chromium(VI) in the leather components of the shoe. The firm indicated that the shoes were distributed for sale in September 2010 and that around 20,000 pairs were sold in their 18 European country stores. The effects of chrome VI therefore prompted the recall of C&A baby shoes from the stores as indicated earlier (Anonymous 2011). The formation of such potentially toxic contents in all leather products exhibited, through bodily contact, a serious impact to human health either directly or indirectly (Cot et al. 2008).

Currently, almost 90% of the manufactured leather products are tanned with chromium (III) salts as they impart positive characteristics to leather (Covington 2009). Although Cr(VI) is not directly used during leather production, but due to the ageing process of leather products with time due to the influence of various environmental conditions such as heat, light, and humidity, Cr⁺³ in leather may oxidize into Cr⁺⁶ (Colak and Dandar, 2010). Various fatliquoring agents, retanning agents, and factors such as pH etc. may potentially cause Cr⁺⁶ formation in leather. During the degradation process which occurs due to the effects of temperature and UV lights, the fatliquoring agents, tanning agents, and auxiliary agents replace molecules of the leather structure and free radicals are subsequently formed. As a result of these radicals created there is a potential tendency, for Cr⁺³ to oxidize to Cr⁺⁶ (Puntener 1996). However, phenolic components block these formed free radicals and prevent oxidation, thus eliminate the risk of Cr⁺⁶ formations. As a matter of fact, antioxidants are defined as the components which delay or prevent the oxidation of the substrate by stabilizing, deforming free radicals or delay or

prevent the oxidation of the substrate by chelating metals (Antolovich et al. 2002, Çam et al. 2009). Blocking of free radicals by phenolic components is shown in Figure 1.

For the maximum Cr⁺⁶ amounts, which may be included in leather products, various countries have determined limit values between 3 and 50 ppm. Nevertheless, the EU Commission recommended 10 ppm as the limit value for all leathers and leather products (Anonymous 2002). Due to all these limitations, companies determine the chromium(VI) amount which may occur in different types of leather they manufacture through various accelerated ageing processes. The increasing chromium(VI) amount above the defined limit values as a result of ageing, prevents companies from obtaining an Eco-leather label. In addition to Cr(VI), a formaldehyde problem which occurs in the leathers also causes serious problems for companies.

Various studies have been conducted in order to prevent formaldehyde and chromium (VI) formation in leather products. For this purpose, agents with antioxidant characteristics are used in general (Colak and Dandar 2010, Yu et al. 2010, Bayramoglu et al. 2011). Natural products with antioxidant characteristics are also used in different fields other than the leather industry. For example, certain studies have been conducted with certain herbs regarding the prevention of Cr⁺⁶ formation in waste waters (Owlad et al. 2009, Wang et al. 2009).

The aim of this study was to examine chromium(VI) formation on finished leathers exposed to accelerated ageing conditions such as a temperature of 80°C and a temperature of 80°C with UV and how the used natural extracts during the retanning process affect the chromium(VI) formation in leather under these conditions compared with the control samples (without any extracts).

MATERIALS AND METHODS

Materials

In the study, chrome-tanned wet-blue sheep skins were used as the leather material. The leathers were finished and thereafter processed into a garment. The plant types used including the regions where they were picked are given in Table 1. The thyme used in the study is registered at the Herbarium Center of Ege University with the number EGE 40770.

Methods

Extraction Process

The plants picked from various regions were first dried and then ground. After grinding, the plants were rested in water for 12 hours, and the extraction process was performed the next day after 12 hours. The extraction parameters for each plant are given in Table 2.

After the extraction process, the water was removed by maintaining the solution at 80°C for 48 hours in a drying oven. After drying, a powder extract was obtained. The extraction yield for each plant was calculated in accordance with the following formula (Liu et al., 2010).

Extraction yield (%) = (the amount of powder extract/sample mass) × 100

Processes with Plant Extracts

After the fatliquoring and dyeing processes, the leather samples were processed separately with each plant extract for 45 minutes in the retanning stage. In order to make a comparison in the analyses, a leather sample was manufactured without any extract. The manufacturing process of the leather is shown in Table 3.

Ageing Process

In many studies, the ageing process is implemented for 24 hours at 80°C, and the Cr (VI) amount which occurs in leather is identified (Colak and Dandar 2010). In this study, in addition to the ageing condition mentioned, tougher conditions were instituted to facilitate different ageing process with new treatment regimes, in order to form a higher amount of chromium(VI) in the leather and see more clearly the effects of the herbal extracts used. Leathers were aged in a heat-adjustable UV cabinet (UV light of 254 nm) at 80°C and under UV for 24h and 72h periods and chromium(VI) formation was thus enabled in the sample leather. In order to ascertain the comparative analysis and determine how the herbal extracts influenced the

Table 1. The plants used in the study and picking regions.

Plant type	Picking regions
Hazelnut shells (<i>Corylus avellana</i>)	Duzce, Turkiye
Thyme (<i>Coridothymus capitatus</i>)	Cesme Alacati, Izmir
Olive shoots (<i>Olea europaea</i>)	Buca, Izmir
Walnut leaves (<i>Juglans regia</i>)	Zeytinbagi, Bursa

Table 2. The parameters of the extraction process.

Plant type	Extraction temperature (°C)	Extraction time (hour)
Hazelnut shells	100	6
Thyme	100	2
Walnut leaves	75	2
Olive shoots	75	2

Table 3. The recipe for leathers.

Process	%	Product	Temperature (°C)	Time (min.)	pH
Washing	300	Water	30		
	0.3	Degreasing agent		60	
Drain & Wash					
	300	Water	35		
	2	Chromium salt			
	2	Synthetic tanning agent			
	2	Chrome syntan		60	
Neutralization	1	Sodium formate		60	
	2	Sodium bicarbonate		2x10+60	5.5-6.0
Drain & Wash					
Dyeing-Fatliquoring-Retanning	150	Water	40		
	3	Dyestuff		35	
	+70	Water	70		
	6	Natural fatliquor agent*			
	4	Synthetic fatliquor agent*		60	
	3	Resin tanning agent		30	
	4	Plant extract**		45	
	1	HCOOH		30	3.8-4.0
Drain & Wash					
Horsing					
Drying					

* Fatliquor agents used were emulsified.

** Plant extract wasn't used for control samples

chromium(VI) formation in leather, subsequent ageing process on leather was evaluated. Also as a control, leather samples tanned into a finished product, with no treatment with any extracts, was compared with other treated samples to determine the significant experimental effects.

Chromium(VI) Analysis on Leather Samples

The chromium(VI) analysis of leather samples was conducted at 540 nm with a Shimadzu UV-1601 PC UV-Visible brand spectrophotometer according to the IUC 18 (EN ISO 17075) standard method (Anonymous 2007). The analysis was replicated twice.

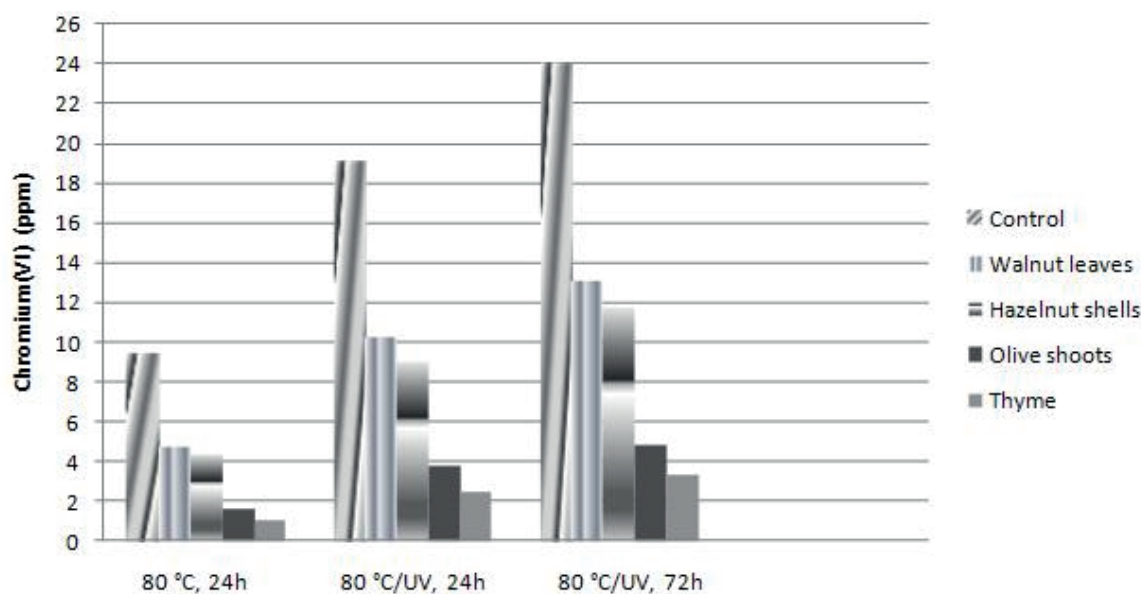


Fig. 2. The effects of the plant extracts used on Cr(VI) formation.

RESULTS

Extraction Yield

The extraction yield obtained from each plant is seen in Table 4.

When Table 4 is examined, it is seen that the highest extraction efficiency was obtained from walnut leaves with 17% and the lowest from hazelnut shells.

Chromium (VI) Amounts in Leather Samples

Various suggestions are introduced and the related studies are ongoing in order to prevent chromium(VI) formation in leather. For example, Yu et al. (2010) reported that phenolic compounds had an inhibitory effect on the oxidation of oleic acid influencing the oxidation of Cr(III) into Cr(VI). Çandar et al. (2008) stated that the increase in the amount of double bond in the fatliquoring agents played a fundamental role in Cr(VI) formation. Therefore, the products containing phenolic compounds and more reliable fatliquoring agents should be used in order to reduce the possibility of Cr(VI) formation. In their study, Colak and Dandar (2010) used tannic acid with antioxidative characteristics during different processes of leather manufacturing to reduce the Cr(VI) formation amount in leather due to ageing. Similar to our study, Font et al., (1999) revealed in their study that the employed antioxidant agents

Table 4. Extraction yield for each plant.

Plant type	Extraction yield (%)
Hazelnut shells	3.3
Thyme	12
Walnut leaves	17
Olive shoots	11.6

Table 5. Cr(VI) amounts identified in the leather samples after the ageing process.

Extract type	80 °C, 24h		80 °C/UV, 24h		80 °C/UV, 72h	
	Cr(VI) Amount (ppm)	Reduction Rate	Cr(VI) Amount (ppm)	Reduction Rate	Cr(VI) Amount (ppm)	Reduction Rate
Control sample	9.39	-	19.08	-	24.02	-
Walnut leaves	4.76	49.31%	10.22	46.44%	13.04	45.71%
Hazelnut shells	4.32	54%	8.98	52.94%	11.76	51%
Olive shoots	1.54	83.6%	3.81	80%	4.8	80%
Thyme	1.01	89.24%	2.42	87.3%	3.31	86.2%

reduced chromium(VI) formation in leather. Babu et al. (2005) managed to eliminate hexavalent chromium in leather by using sodium bisulfite and tetrakis-hydroxymethylphosphonium sulphate (THPS).

In this research, an attempt was directed towards reducing chromium(VI) formation in leather to Cr(VI) as in an identified leather sample processed with herbal extracts with antioxidative characteristics. This along with the control sample are as shown in Table 5.

Upon the examination of Table 5; leathers processed with walnut leaves, hazelnut shells, olive

shoots, and thyme extracts indicated a significant decrease in chromium(VI) amounts when compared to the control sample as observed under all three ageing conditions. However, the best elimination was obtained with thyme extract. With thyme extract 89.24% reduction was obtained at 80°C for the 24h ageing condition, 87.32% was observed at 80°C/UV for the 24h ageing condition, and 86.22% at 80°C/UV for the 72h ageing condition. The effect of the herbal extracts as demonstrated slightly decreased percentage wise as the severity of ageing conditions increased as can be seen in Table 5.

In parallel to our study, Owlad et al. (2009) managed to prevent Cr(VI) formation in waste waters with hazelnut shell. Also, Wang et al. (2009) achieved the removal of chromium(VI) from an aqueous solution using walnut hull. These studies indicated that natural products could be used in various processes. The findings of the current study are shown in Figure 2.

In light of the findings of our research, the percentile risk of Cr(VI) formation due to ageing during the lifetime of the leather products can greatly be reduced especially through the use of thyme extract during the retanning stage of the leather process, thus addressing the pertinent issues associated with Cr(VI).

DISCUSSION AND CONCLUSION

The impacts of the chemical agents used during

leather processing on human and environmental health are continuously being debated and such related studies are still ongoing. Restrictions are introduced regarding the use of harmful chemicals for human and environmental health. For example, chromium(VI) is considered as the leading toxic agent. Measures are taken to prevent chromium(VI) formation in leather, recommendations are issued and studies are conducted in order to eliminate or reduce chromium(VI) formation in leather by using various chemicals.

Previous studies explained that the herbs used in this study have antioxidative characteristics (Namiki 1990, Pereira et al. 2007, Contini 2008). Significant results therefore have been achieved in this research regarding the reduction of chromium(VI) formation in leather exploiting the antioxidative properties of herbal extracts. The study further demonstrated that different extraction methods used in obtaining herbal extracts with varying ratios of the extracts used and subsequent combination of extracts will impart different effects on the reduction of Cr(VI). Through this study, it is envisioned that the results obtained would highly contribute to ecological leather production, providing a basis for further research and improve on the current knowledge base.

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