

Valorization of Pomegranate Peel Waste as Retanning Agent in Leather Industry and Investigation of Its Effect on Prevention of Cr(VI) Formation

by

Çiğdem Kılıçarışlan Özkan

Faculty of Engineering, Department of Leather Engineering, Ege University, 35100 Bornova, Izmir, Turkey

Abstract

Although Cr(VI) is not used in any step of the manufacturing process, the entity of Cr(VI) in leather and leather products has become a concern in the leather industry. Formation of free radicals may bring about conditions for the oxidation of free Cr(III) (if exists in leather) to Cr(VI) and these oxidations are usually catalyzed by heat and UV radiation. Antioxidants have an important role in order to inhibit oxidant compound activity by donating an electron to compounds. There are many studies on the prevention of Cr(VI) formation in leather production. The inhibiting properties of Cr(VI) formation were usually investigated by using commercial vegetable tannins (polyphenols) together with other retanning agents in retanning process. However, no study has been conducted on the possible use of pomegranate peel tannins as an alternative retanning agent, which is known as an important source of antioxidants, in leather making and their ability to prevent Cr(VI) formation. In the present study, pomegranate peels were extracted in different solvents and total phenolic content and antioxidant power of the extracts were determined by Folin-Ciocalteu, FRAP (The Ferric Reducing Ability of Plasma) and TEAC/ABTS (Trolox-Equivalent Antioxidant Capacity/2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid)) methods. Furthermore, different amounts of pomegranate peel extracts were used in retanning processes and the leathers were investigated in terms of increases in thickness, color changes as well as effect on prevention of Cr(VI) formation. The results revealed that besides noticeable retanning performance, pomegranate peel extract has a spectacular effect on prevention of Cr(VI) formation as compatible with its antioxidant power.

Introduction

Chrome tanning is the most favored technology in the leather industry worldwide due to its ability to produce leather with attributes desirable for high-quality leather such as excellent hydrothermal stability, better dyeing characteristics and softness. So much so that today approximately 80-90% of leather tanned is chromium based. However, the technology has come under censure globally for its severe environmental impacts and adverse effects on human health and other organisms.¹ Cr(III) salts, mainly

chromium (III) hydroxide sulphate ($\text{Cr}(\text{OH})\text{SO}_4$), are ordinarily used in the chrome tanning process. Although Cr(VI) compounds are not used in tanning process, the chemicals used in production and other factors such as a chemical reaction facilitated by heat, UV radiation, changes in pH and oxidizing agents etc., may cause oxidation of Cr(III) to Cr(VI) upon ageing of leather products. These deformations generally emerge due to the oxidant group free radicals, which are dependent on these factors.² Antioxidants interact with free radicals, terminating the adverse chain reactions and converting them to harmless products.³ Plant-derived antioxidants (vegetable tannins) are active substances obtained from natural plants through extraction and sometimes purification techniques.⁴⁻⁶ They mainly include polyphenols, flavonoids, terpenoids and aromatic compounds and their composition can vary widely depending on the characteristics of the plants and the extraction procedures.^{5,6}

Vegetable tannins (plant-based polyphenols) are used in tanning and retanning processes in leather making due to the fact that they are water soluble and easily interact with collagen predominantly via multiple hydrogen bonds. Mimosa, quebracho, sumac, tara, valonea and chestnut are the most common vegetable tannins used commercially for this purpose. In recent years, researchers have attempted to explore the use of new plant materials for tanning/retanning processes.⁷⁻¹¹ However, there is no report regarding the use of pomegranate peel extract as a retanning agent in leather making for prevention of Cr(VI) formation.

Pomegranate (*Punica granatum* L.) belongs to Punicaceae family and it is an important fruit crop adaptable to a wide range of agro-climatic conditions. Pomegranate fruit is mainly grown in Iran, Tunisia, Turkey, Spain, Egypt, Morocco, USA, China, India, Argentina, Israel and South Africa.^{12,13} Pomegranate peel (PoP) includes approximately 30–40% portion of the pomegranate fruit and remains as a byproduct after juicing the fruit.^{13,14} Large parts of fruits are wasted in processing industries (which can amount to fifty percent in case of pomegranate) causing environmental pollution. PoP is considered a waste, however it is composed of notable polyphenolic compounds such as phenolic acids, anthocyanins and tannins (ellagitannins, punicalagin, punicalin and gallotannins).¹⁵ PoP color is primarily due to the presence of anthocyanins (one class

of flavonoids).^{13,16} Owing to this, it possesses a higher antioxidant activity than the edible portion (arils).^{13,17,18} Indeed, PoP holds significant free radical scavenging, anti-microbial, antiatherogenic and antimutagenic properties.¹⁹⁻²³ Therefore, PoP should be considered as a co-product with juice extraction and not a waste.^{15,24} In recent years, there has been an increase in interest for beneficial phytochemicals present in fruit peels and utilization of them in food, pharmaceutical and cosmetic industries.¹³

The aim of this study is to investigate the possible utilization of pomegranate peels as a valuable new source of tannin for leather industry.

Materials and Methods

Materials

The pomegranate peels used in the trials were supplied from a food company operating in Torbali/Izmir. The peels were rinsed with distilled water so as to remove dirt (dust, mud etc.). Then they were dried in ambient conditions for one day, and then in an oven at 40°C for two days. The dried peels were broken into pieces of about 0.5-1 cm and kept dry, in the dark, and at ambient temperature.

Wet-blue sheep leathers (breed of Métis) were used in retanning experiments.

Methods

Determination of moisture content of pomegranate peels: The moisture content of pomegranate peels was determined according to SLC 113²⁵ test method with three replications and mean data was given as result.

Preparation of extracts: 20 g dehumidified pomegranate peels were pre-soaked overnight in 400 mL distilled water before the extraction process. In order to determine the effect of temperature on extraction efficiency and tannin content, pomegranate peels were subjected to Koch extraction separately for 8 h at 70°C and 90°C. Water was used as solvent in the extractions.

Determination of maximum extractable materials (MEM) from pomegranate peels: Maximum extractable material from pomegranate peels was determined according to the method described by Sivakumar et al.²⁶ with slight changes. Twenty grams of pomegranate peels were soaked in 400 mL of distilled water (Float-I) in a clean flask and magnetically stirred at constant temperatures of 70°C and 90°C for 8 h, separately. The flask was covered with aluminum foil to prevent water evaporation.

Extract solution was filtered after 8 h, then the total solids of Float-I was determined. Remaining pomegranate peels were re-extracted similarly for following two days, and samples were taken every day

after 8 h of extraction and total solids were also determined for each filtered extract solution (Float II and Float III). The total maximum soluble material per gram of the pomegranate peels was calculated as MEM.

Determination of extraction yields and tannin contents of extract solutions: Extraction yields and tannin contents of solutions obtained from both Koch extractions and MEM experiments (total solutions collected in 3 days) were determined.

Extraction yields were calculated according to the Formula 1. The extraction trials were repeated three times and mean data were given.

$$(\%) \text{ Extraction Yield} = (\text{extract obtained (g)} / \text{pomegranate peels used (g)}) \times 100$$

(Formula 1)

The pomegranate peel extracts were analyzed to determine the amounts of total solids (SLC 114²⁷), total solubles (SLC 115²⁸), non-tannin content (SLC 116²⁹), and tannin matter absorbable by hide powder (SLC 117³⁰). Analyses were performed in triplicate and mean data were given.

Total phenols and antioxidant powers of pomegranate peels: Before the analyses, pomegranate peels were ground using a tilting grinder machine (Super Mixer SM 108 Model). A 0.1 g sample of pomegranate peel powder was extracted overnight in 100 mL of solvent in dark ambient before the total phenol and antioxidant analyses. In order to determine the possible effects of different solvents on extractable total phenols and correspondingly antioxidant power of pomegranate peels, water (100 mL) and water:ethanol (50:50 mL), water:methanol (50:50 mL), water:acetone (50:50 mL) mixtures were used as solvent. All analyses were carried out with two replications.

The total phenolic content of pomegranate peels was determined by Folin-Ciocalteu method, which was adapted from Swain and Hillis³¹, at 725 nm with a spectrophotometer (Shimadzu UV-1601 Spectrophotometer) and quantification was done on basis of the standard curve of gallic acid concentration ranging between 15 and 400 µmol/L ($r^2=0.9929$). The amount of the total phenolic content is expressed as mg of gallic acid equivalent (GAE) in g extract.

As is known, there is no single universal method to reliably investigate antioxidant powers of plant materials. Therefore FRAP (Iron (III) Reducing Antioxidant Power)^{2,32,33} and TEAC/ABTS (Trolox Equivalent Antioxidant Capacity)^{2,34} methods were used in order to obtain comparable and reliable results for determining antioxidant and antiradical activities of pomegranate peel extracts.

In the method of Trolox Equivalent Antioxidant Capacity (TEAC/ABTS), the antioxidant activity of pomegranate peel extracts

was determined at 734 nm with a spectrophotometer and the quantification was performed according to the standard curve of Trolox concentration ranging between 100 and 1500 $\mu\text{mol/L}$ ($r^2=0.9943$). FRAP method was also carried out in the same way, standard curve was obtained with Trolox ranging from 100-1200 $\mu\text{mol/L}$ ($r^2=0.9970$), UV measurements were done at 593 nm. In both methods, the antioxidant power is expressed as mg of Trolox equivalent (TE) in g extract.

Usage of extract solutions in retanning process: From the comparison of yields and tannin contents of extract solutions obtained from Koch extractions performed at 70°C and 90°C, it was seen that there was no remarkable difference. Therefore, it was decided to use the solutions obtained at 70°C in retanning processes.

The coupon areas of wet-blue leathers were divided into 30x30 cm pieces as experimental samples. Pomegranate peel extracts were used at 1%, 2.5%, and 5% dry matter on the wet-blue leather weight and two leather pieces were used for each process. The retanning process was prescribed in Table I. The extract solution was not used in control samples.

Post-Retanning Tests

Determination of filling coefficient: In order to determine changes in the thickness of retanned leathers depending on different ratios of extract solution usage, the thicknesses of the leathers from 10 different areas were measured in wet form before retanning (T_1) (after neutralization) and after retanning (T_2) according to ISO 2589³⁵. Filling coefficients were calculated according to Formula 2.

$$(\%) \text{ Filling coefficient} = ((T_2 - T_1) / T_1) \times 100 \quad (\text{Formula 2})$$

Determination of color changes: The color differences of leathers retanned with different ratios of pomegranate peel extracts were determined by using Minolta CM-2600d spherical spectrophotometer with CIE 100 standard observer angle and CIE standard D65 daylight source. The colors of all retanned leather samples and their color differences against the control sample were evaluated according to the CIE Lab color coordinate system.

Artificial ageing of leather samples and Cr (VI) analysis: Pomegranate peel extracts' possible effects on prevention of Cr(VI) formation were investigated. First of all, the initial Cr(VI) contents of control and pomegranate peel extract retanned leather samples were determined. Then, two ageing methods were used in order to

Table I
Retanning recipe

Process	Amount (%)	Product	Temperature (°C)	Duration (min.)	pH
Washing	200	Water	35		
	0.2	HCOOH		30	
Draining					
Neutralization	150	Water	35		
	0.5	Neutralizing syntan	35	15	
	0.3	NaHCO ₃		45	5.5-6.0
Draining					
Washing	200	Water	35	30	
Draining					
Retanning	150	Water	40		
	x	Extract solution		20	
Fatliquoring	3	Sulphited fish fatliquor	45	45	
	3	Sulphited natural fatliquor			
	2	Synthetic fatliquor			
	1	Synthetic paraffin			
Fixation	1	HCOOH		30	
	0.2	HCOOH		30	3.5
Washing	200	Water	35	20	

determine Cr(VI) formation under thermal pre-ageing and drastic conditions. In the first method, the leather samples were subjected to the thermal pre-ageing (80°C for 24 h) procedure according to the ISO 10195³⁶ standard. In the second method², leather samples were exposed to UV light (360 nm) and kept at 80°C for 7 days. Cr(VI) analysis was performed immediately on the leathers which were cooled after the ageing processes. Cr(VI) contents in leathers were determined according to the ISO 17075-1³⁷ test method.

Results and Discussion

Moisture Content, Extraction Yields and Tannin Contents of Pomegranate Peels: Moisture content of pomegranate peels was found to be 5.5(±0.2)%.

As a result of the trials on the MEM of pomegranate peels; it was determined that the increase in temperature caused a significant increase in extractable total solids, while the share of tannins in the solids decreased noticeably (Table II). As a matter of fact, this situation showed that the increasing temperature in MEM trials caused a significant increase in the quantity of non-tannins transferred to the solution rather than the quantity of tannins.

However, from the Koch extraction of pomegranate peels at different temperatures, a slight increase in the amount of total

solids and tannins extracted (Table II) was determined by increasing temperature. But, since this increase was not very significant and considering the possible negative effects of high temperatures in extraction on the chemical structures of tannins, it was decided to use parameters of 70°C and 8 h in the extraction of pomegranate peel extracts that were used in the retanning experiments.

Total phenolic contents and antioxidant powers of pomegranate peels: Considering the total phenolic contents of pomegranate peel extracts; the highest amount of phenolics was obtained by using water:methanol mixture as solvent, followed by water:acetone, water:ethanol and water (Table III). Similarly, Orak et al.³⁸ determined the total phenolic contents of pomegranate peels, which extracted in water, methanol, and ethanol, between 126.11-212.48 µg GAE/mg in extract, to be the lowest value in water and the highest value in methanol extraction.

The antioxidant powers of the pomegranate peels, extracted in different solvents, according to ABTS and FRAP methods were shown in Table III. It is clearly seen that the highest antioxidant power was obtained from water:acetone extraction in both methods. Singh et al.¹³ remarked that there seems to be close relationship between antioxidant power and the levels of phenolic compounds extracted by using different solvents. Abid et al.³⁹ reported that acetone extraction of pomegranate peels exhibited

Table II
The effect on extraction yields and tannin contents of different extraction temperatures

Extraction Temperature (°C)	Koch Extractions		MEM Extractions	
	Extraction Yield (Total Solids) (%)	Tannin Content (%)	Extraction Yield (Total Solids) (%)	Tannin Content (%)
70	43.4(±0.3)	53.8(±0.2)	55.3(±0.4)	53.7(±0.4)
90	45.5(±0.4)	54.5(±0.2)	67.1(±0.5)	40.8(±0.3)

Table III
Total phenolic contents and antioxidant powers of pomegranate peels extracted in different solvents

Type of Solvent	Total phenolic content (mg GAE/g)	Antioxidant power according to ABTS (mg TE/g)	Antioxidant power according to FRAP (mg TE/g)
Water	116.3(±1.2)	554.1(±13.3)	511.8(±16.5)
Water:Ethanol	136.0(±3.5)	645.3(±6.7)	547.1(±5.3)
Water:Methanol	208.8(±4.0)	840.6(±3.7)	573.7(±1.9)
Water:Acetone	195.1(±2.4)	885.5(±7.2)	577.3(±1.9)

the highest antioxidant activity (97.82% according to the DDPH method) as compared to water and ethanol extract. On the other hand, Elfalleh et al.⁴⁰ determined that methanolic pomegranate peel (7.5 TEAC mmol/100 g DW) exhibited higher ABTS activities than aqueous one (3.80 TEAC mmol/100 g DW) and indicated that these differences were due to the content and quality of the phenolic compounds extracted in different solvents.

Filling coefficient and color changes of retanned leathers: Filling coefficient test results of the leathers retanned with 1, 2.5, and

5 % pomegranate peel extract were given in Table IV. From the evaluation of the results, it was seen that the thicknesses of the leathers increased for all samples in conjunction with increasing amount used in retanning. The maximum increment in filling coefficient was determined to be 10.6% with 5% pomegranate peel ratio which can be considered as a remarkable solo performance for retanning.

Depending on their chemical structures, colors and percentages of use, retanning agents cause changes in leather physical properties (fullness, firmness, color, handle etc.). Together with other properties, the color imparted by retanning agents to the leather is important, as it has a direct effect on dyeing and the final color. That's why the color of the leathers retanned with pomegranate peel extracts was measured. The data of the color measurements of the leathers retanned with pomegranate peel extracts and comparisons with control sample were given in Table V. Color measurement of leathers was performed before and after ageing. Unretanned and unaged leather was used as control sample. From the examination of the data, regardless of the amount of pomegranate peel used in retanning, it was observed that the color of the leathers significantly shifted towards yellow and slightly shifted towards green compared to the control sample. There was

Table IV

Filling coefficient values of retanned leathers

Pomegranate peel amount used in retanning	Filling coefficient (%)
Control Sample	0.6(±0.3)
1 %	5.0(±0.7)
2.5 %	8.0(±1.1)
5 %	10.6(±0.9)

Table V

Color measurement values of leathers retanned with pomegranate peel extracts at different ratios before and after ageing

Sample	L	a	b	dL	da	db	dE
Before Ageing							
Control Sample	81.56	-4.22	0.47	-----	-----	-----	-----
1 %	77.19(±1.0)	-5.90(±0.5)	20.05(±0.5)	-4.37(±1.0)	-1.68(±0.5)	19.58(±0.5)	20.16(±0.6)
2.5 %	77.44(±0.9)	-5.02(±0.2)	19.31(±0.7)	-4.11(±0.9)	-0.80(±0.2)	18.83(±0.7)	19.31(±0.8)
5 %	74.55(±1.0)	-4.42(±0.1)	19.77(±0.5)	-7.01(±1.0)	-0.20(±0.1)	19.30(±0.5)	20.55(±0.7)
After Ageing (80 °C for 7 days with UV light)							
Control Sample	83.56(±1.1)	-3.72(±0.3)	0.87(±0.4)	2.01(±1.1)	0.50(±0.3)	0.40(±0.4)	2.17(±1.1)
1 %	77.86(±0.7)	-5.09(±0.2)	20.62(±0.7)	-3.70(±0.7)	-0.87(±0.2)	20.15(±0.7)	20.51(±0.8)
2.5 %	76.90(±0.9)	-4.66(±0.3)	20.37(±0.5)	-4.66(±0.9)	-0.43(±0.3)	19.90(±0.5)	20.45(±0.6)
5 %	75.17(±0.8)	-4.13(±0.1)	20.89(±0.6)	-6.39(±0.8)	0.10 (±0.1)	20.42(±0.6)	21.41(±0.8)

Where: L: lightness / brightness (L=0 black, L=100 white), a: red/green color (+a red, -a green), b: yellow/blue color (+b yellow, -b blue) and dL, da, db and dE the changes in color compared to the control sample.

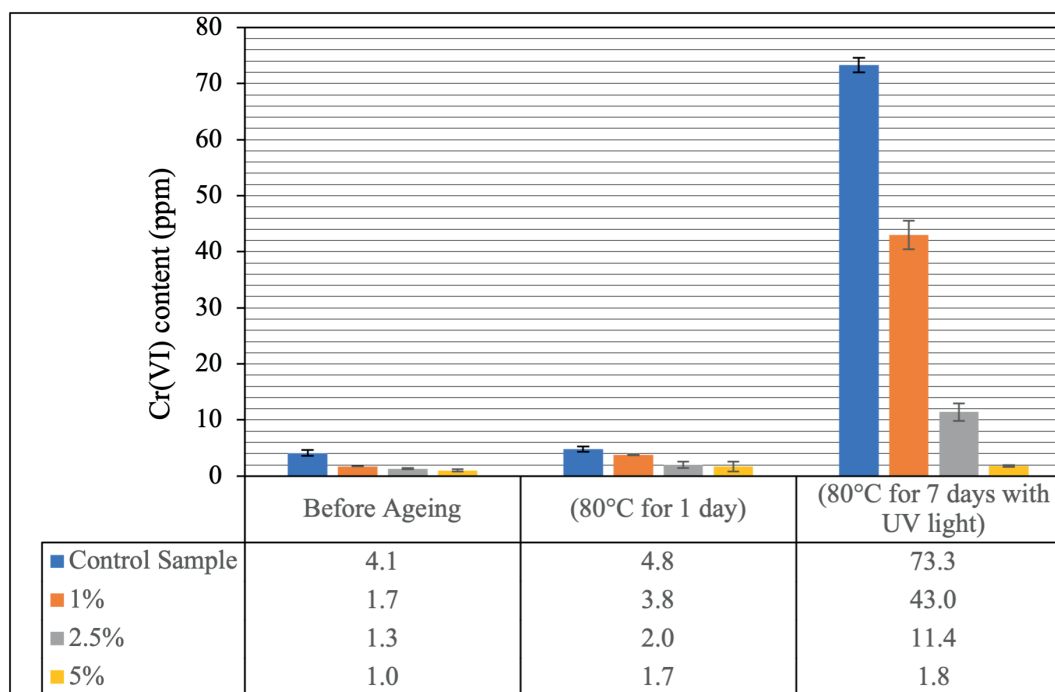


Figure 1. Comparison of Cr(VI) levels for leather samples retanned with different amount of pomegranate peel extracts.

no remarkable alteration in the color and shade of the retanned leathers by ageing.

Cr(VI) contents of leather samples: In order to determine Cr(VI) formation preventing effect of pomegranate peel extract use in retanning, the Cr(VI) contents in control samples and the leather samples retanned with pomegranate peel extract were measured before and after ageing treatments (Figure 1).

Considering the values regarding the Cr(VI) content of the leathers before and after pre-ageing (80°C for 1 day); the decrease in the Cr(VI) content of the samples in parallel with the increasing use of pomegranate peel extract drew attention. However, the most striking result emerged in the data obtained after ageing under drastic conditions. As a matter of fact, 73.3 ppm of Cr(VI) resulting from drastic ageing in the control sample decreased to 43, 11.4 and 1.8 ppm in the leather samples retanned with 1%, 2.5% and 5% of pomegranate peel extract respectively. Thus, it was determined that the use of pomegranate peel extract in retanning, effectively suppressed/prevented the formation of Cr(VI) in the leathers via its strong antioxidant effect.

Conclusions

In the present study, pomegranate peels which arise as waste in fruit juice enterprises were investigated in terms of total phenolic

contents and antioxidant powers as well as the pomegranate peel tannins' retanning performances and Cr(VI) preventing effect. Considering the analysis results, while the highest phenolic content was found to be 208.8 mg GAE/g using a water:methanol extraction, the highest antioxidant powers were found to be 885.5 and 577.3 mg TE/g using a water:acetone extraction both for ABTS and FRAB methods, respectively.

Regarding pomegranate peel tannins' retanning and Cr(VI) preventing performances; the increase in the thicknesses (5, 8 and 10.6%) of the leathers which were retanned with 1, 2.5 and 5% of pomegranate peel extract can be regarded as a remarkable solo performance for retanning. Considering the data obtained from the experiments/analysis on Cr(VI) prevention; even in mild ageing conditions the decrease in the Cr(VI) content of the leather samples, in parallel with the increasing use of pomegranate peel extract drew attention. However, the suppression of very high amounts of Cr(VI) - such as 73.3 ppm arising under drastic ageing conditions - revealed that the use of pomegranate peel extract in retanning strongly suppressed/prevented the formation of Cr(VI) in the leathers.

The findings revealed that pomegranate peels can be utilized in leather production as a valuable new source of tannins with their high phenolic content, antioxidant powers and significant Cr(VI) inhibition effects.

References

- China, C.R., Maguta, M.M., Nyandoro, S.S., Hilonga, A., Kanth, S.V., Njau, K.N.; Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review. *Chemosphere* **254**, 126804, 2020. <https://doi.org/10.1016/j.chemosphere.2020.126804>
- Kilicarislan Ozkan, C., Ozgunay, H., Kalender, D.; Determination of antioxidant properties of commonly used vegetable tannins and their effects on prevention of Cr(VI) formation. *J Soc Leather Technol Chem* **99(5)**, 245-249, 2015.
- Khalil, I., Yehye, W.A., Etxeberria, A.E., Alhadi, A.A., Dezfooli, S.M., Julkapli, N.B.M., Basirun, W.J., Seyfoddin, A.; Nanoantioxidants: Recent trends in antioxidant delivery applications. *Antioxidants* **9(1)**, 24, 2020. <https://doi.org/10.3390/antiox9010024>
- Dong, Z., Xu, F., Ahmed, I., Li, Z., Lin, H.; Characterization and preservation performance of active polyethylene films containing rosemary and cinnamon essential oils for Pacific white shrimp packaging. *Food Control* **92**, 37-46, 2018. <https://doi.org/10.1016/j.foodcont.2018.04.052>
- Figueroa-Lopez, K.J., Vicente, A.A., Reis, M.A.M., Torres-Giner, S., Lagaron, J.M.; Antimicrobial and antioxidant performance of various essential oils and natural extracts and their incorporation into biowaste derived poly(3-hydroxybutyrate-co-3-hydroxyvalerate) layers made from electrospun ultrathin fibers. *Nanomaterials* **9(2)**, 144, 2019. <https://doi.org/10.3390/nano9020144>
- Zhang, Y., Wang, B., Lu, F., Wang, L., Ding, Y., Kang, X.; Plant-derived antioxidants incorporated into active packaging intended for vegetables and fatty animal products: A review. *Food Addit Contam Part A*, **38(7)**, 1237-1248, 2021. <https://doi.org/10.1080/19440049.2021.1885745>
- Frederik, H., Romer, A., Nadine, S., Susan, I., Bonnet, D., David, R., Dan, V.; Tanning fingerprint in vegetable tanned leather by solid state NMR spectroscopy and comparison with leather tanned by other processes. *Molecules* **16(2)**, 1240-1252, 2011. <https://doi.org/10.3390/molecules16021240>
- Isam, E., Christina, Y.; Determination of tannins of three common acacia species of Sudan. *J Adv Chem* **9**, 25-30, 2014. <http://doi.org/10.1155/2014/192708>
- Mohammed, S.A., Rames, C., Madhan, B., Demessie, B.A.; Extraction of bio-active compounds from Ethiopian plant material *Rumex abyssinicus* (mekmeko) root-A study on kinetics, optimization, antioxidant and antibacterial activity. *J Taiwan Inst Chem Eng* **75**, 228-239, 2017. <https://doi.org/10.1016/j.jtice.2017.03.004>
- Mohammed, S.A., Naisini, A., Madhan, B., Demissie, B.A.; *Rumex abyssinicus* (mekmeko): A newer alternative for leather manufacture. *Environ Prog Sustain Energy* **39(6)**, e13453, 2020. <https://doi.org/10.1002/ep.13453>
- Badessa, T.S., Hailemariam, M.T., Ahmed, S.M.; Greener approach for goat skin tanning. *Cogent Eng* **9(1)**, 2018959, 2022. <https://doi.org/10.1080/23311916.2021.2018959>
- Kahramanoglu, I., Usanmaz, S.; Pomegranate Production and Marketing, first ed. Boca Raton, USA. CRC Press. 2016. DOI:10.1201/b20151
- Singh, B., Singh, J.P., Kaur, A., Singh, N.; Phenolic compounds as beneficial phytochemicals in pomegranate (*Punica granatum* L.) peel: A review. *Food Chem* **261**, 75-86, 2018. <https://doi.org/10.1016/j.foodchem.2018.04.039>
- Cam, M., Icyer, N.C., Erdogan, F.; Pomegranate peel phenolics: Microencapsulation, storage stability and potential ingredient for functional food development. *LWT-Food Sci Technol* **55(1)**, 117-123, 2014. <https://doi.org/10.1016/j.lwt.2013.09.011>
- Singh, B., Singh, J.P., Kaur, A., Singh, N.; Antimicrobial potential of pomegranate peel: a review. *Int J Food Sci Technol* **54(4)**, 959-965, 2019. <https://doi.org/10.1111/ijfs.13964>
- Zhao, X., Yuan, Z., Fang, Y., Yin, Y., Feng, L.; Characterization and evaluation of major anthocyanins in pomegranate (*Punica granatum* L.) peel of different cultivars and their development phases. *Eur Food Res Technol* **236(1)**, 109-117, 2013. <https://doi.org/10.1007/s00217-012-1869-6>
- Venkataramanamma, D., Aruna, P., Singh, R.P.; Standardization of the conditions for extraction of polyphenols from pomegranate peel. *J Food Sci Technol* **53(5)**, 2497-2503, 2016. <https://doi.org/10.1007/s13197-016-2222-z>
- Amri, Z., Zaouay, F., Lazreg-Aref, H., Soltana, H., Mneri, A., Mars, M., Hammami, M.; Phytochemical content, fatty acids composition and antioxidant potential of different pomegranate parts: Comparison between edible and non edible varieties grown in Tunisia. *Int J Biol Macromol* **104**, 274-280, 2017. <https://doi.org/10.1016/j.ijbiomac.2017.06.022>
- Sestili, P., Martinelli, C., Ricci, D., Fraternali, D., Bucchini, A., Giamperi, L., Curcio, R., Piccoli, G., Stocchi, V.; Cytoprotective effect of preparations from various parts of *Punica granatum* L. fruits in oxidatively injured mammalian cells in comparison with their antioxidant capacity in cell free systems. *Pharmacol Res* **56**, 18-26, 2007. <https://doi.org/10.1016/j.phrs.2007.02.003>
- Aviram, M., Volkova, N., Coleman, R., Dreher, M., Reddy, M.K., Ferreira, D., Rosenblat, M.; Pomegranate phenolics from the peels, arils, and flowers are antiatherogenic: Studies in vivo in atherosclerotic apolipoprotein E-deficient (Eo) mice and in vitro in cultured macrophages and lipoproteins. *J Agric Food Chem* **56(3)**, 1148-1157, 2008. <https://doi.org/10.1021/jf071811q>
- Zahin, M., Aqil, F., Ahmad, I.; Broad spectrum antimutagenic activity of antioxidant active fraction of *Punica granatum* L. peel extracts. *Mutat Res* **703(2)**, 99-107, 2010. <https://doi.org/10.1016/j.mrgentox.2010.08.001>
- Malviya, S., Arvind, Jha, A., Hettiarachchy, N.; Antioxidant and antibacterial potential of pomegranate peel extracts. *J Food Sci Technol* **51**, 4132-4137, 2014. <https://doi.org/10.1007/s13197-013-0956-4>
- Akhtar, S., Ismail, T., Fraternali, D., Sestili, P.; Pomegranate peel and peel extracts: Chemistry and food features. *Food Chem* **174**, 417-425, 2015. <http://dx.doi.org/10.1016/j.foodchem.2014.11.035>

24. Karimi, M., Sadeghi, R., Kokini, J.; Pomegranate as a promising opportunity in medicine and nanotechnology. *Trends Food Sci Technol* **69**, 59-73, 2017. <https://doi.org/10.1016/j.tifs.2017.08.019>
25. SLC-113, Determination of Moisture, Society of Leather Technologists and Chemists, 1996.
26. Sivakumar, V., Ravi Verma, V., Rao, P.G., Swaminathan, G.; Studies on the use of power ultrasound in solid-liquid myrobalan extraction process, *J Clean Prod* **15**, 1813-1818, 2007. <https://doi.org/10.1016/j.jclepro.2006.06.006>
27. SLC 114, Determination of Total Solids, Society of Leather Technologists and Chemists Official Methods of Analysis, 1996.e
28. SLC 115, Determination of Total Solubles, Society of Leather Technologists and Chemists Official Methods of Analysis, 1996.
29. SLC 116, Determination of Non-tannin Constituents, Society of Leather Technologists and Chemists Official Methods of Analysis, 1996.
30. SLC 117, Determination of Tannin Matter Absorbable by Hide Powder, Society of Leather Technologists and Chemists Official Methods of Analysis, 1996.
31. Swain, T., Hillis, W.E.; The phenolic constituents of *Purmus domestica*. I. The quantitative analysis of phenolic constituents. *J Sci Food Agric* **10**, 63-68, 1959. <https://doi.org/10.1002/jsfa.2740100110>
32. Benzie, I.F.F., Strain, J.J.; Ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": The FRAP assay. *Anal Biochem* **239**(1), 70-76, 1996. <https://doi.org/10.1006/abio.1996.0292>
33. Ozgen, M., Rees, R.N., Tulio, A.Z., Scheerens, J.S., Miller, A.R.; Modified 2,2'-azino-bis 3-ethylbenzothiazoline - 6-sulphonic acid (ABTS) method to measure antioxidant capacity of selected small fruits and comparison to ferric reducing antioxidant power (FRAP) and 2,2'- diphenyl-1-picrylhydrazyl (DPPH) methods. *J Agric Food Chem* **54**(4), 1151-1157, 2006. <https://doi.org/10.1021/jf051960d>
34. Miller, N.J., Riceevans, C., Davies, M.J., Gopinathan, V., Miller, A.; A novel method for measuring antioxidant capacity and its application to monitoring the antioxidant status in premature neonates. *Clin Sci* **84**, 407-412, 1993. <https://doi.org/10.1042/cs0840407>
35. ISO 2589 [IULTCS/IUP 4], Leather - Physical and mechanical tests - Determination of thickness, 2016.
36. ISO 10195 [IULTCS/IUC 41], Leather - Chemical determination of chromium (VI) content in leather - Thermal pre-ageing of leather and determination of hexavalent chromium, 2018.
37. ISO 17075-1 [IULTCS/IUC 18-1], Leather - Chemical determination of chromium (VI) content in leather - Part 1: Colorimetric method, 2017.
38. Orak, H.H., Yagar, H., Isbilir, S.S.; Comparison of antioxidant activities of juice, peel, and seed of pomegranate (*Punica granatum* L.) and inter-relationships with total phenolic, tannin, anthocyanin, and flavonoid contents. *Food Sci Biotechnol* **21**(2), 373-387, 2012. <https://doi.org/10.1007/s10068-012-0049-6>
39. Abid, M., Yaich, H., Cheikhrouhou, S., Khemakhem, I., Bouaziz, M., Attia, H., Ayadi, M.A.; Antioxidant properties and phenolic profile characterization by LC-MS/MS of selected Tunisian pomegranate peels. *J Food Sci Technol* **54**(9), 2890-2901, 2017. <https://doi.org/10.1007/s13197-017-2727-0>
40. Elfalleh, W., Hannachi, H., Tlili, N., Yahia, Y., Nasri, N., Ferchichi, A.; Total phenolic contents and antioxidant activities of pomegranate peel, seed, leaf and flower. *J Med Plants Res* **6**(32), 4724-4730, 2012. <https://doi.org/10.5897/JMPR11.995>