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A Research on the Use of Waste Mandarin Peels as Fixing Agents in Leather Production and Its Effects on Ageing and Colour

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ABSTRACT

In this research, the effect of extract obtained from waste mandarin peels on inhibition or retardation of ageing of the leather was investigated. Firstly, mandarin peels were extracted and antioxidant activity of the mandarin peels were detected by using of DPPH method. This antioxidant method is based on DPPH that is a purple stable compound, inhibition with sample compound. Extracted mandarin peel samples were read by spectrophotometer at 517 nm wavelength. At final, antioxidant activity of mandarin extract was determined as 65 µM TE/g. The mandarin extract treated with leather after formic acid fixation as a fixator. Goat leathers were kept under 80°C/UV for 72 hours for aging process and the colour values of initial and hindermost leathers were measured with using of Konica Minolta CM 3600d Brand spectrophotometer. *L**, *a**, *b** and ΔE values of the samples were calculated. At the end of the study, it was found that mandarin extract was a natural antioxidant and if it was used as a fixator it could have aging retardant effect at the leather production. Also, it was determined that the use of waste mandarin peels extract increases the brightness of the leather. The difference between the colour values of the leather samples in which the extract was used and not used was found statistically significant.

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Introduction

Nowadays, the importance of organic production and organic products is increasing daily. Restrictions and regulations are introduced on behalf of both human health and environmental pollution due to the negative effects caused by some chemicals used in the waste unit during the leather processing process. In this context, innovative 100% organic leather processing materials are needed. Countries with high agricultural production rate evaluate these products in different forms. The importance of organic products is increasing. The use of organic products has also increased in the leather industry, too (Bayramoğlu et al., 2006; Bayramoğlu, 2006; Bayramoğlu; 2007; Bayramoğlu, 2010). Many agricultural products are exported abroad and provide inputs to our country's economy and one of them is the citrus fruits. Companies producing citrus canned in our country are not evaluated economically for citrus peels such as mandarin and grapefruit which are left after production and this can cause environmental pollution. For example, the Zumdieck Canned Food Company in Salihli has processed about 14 thousand tons of citrus fruits in the past year. By weight 9500 tons of mandarin, 3500 tons of grapefruit and 1000 tons of orange were processed. These products are boiled and sliced one by one, and the slices are turned into "segment preserves". Orange peels are sold to sugarcane and chocolate dressers at good prices. However, about 3000-3500 tons of mandarin peels and 1000-1500 tons of grapefruit peels can't be evaluated at all. Some companies are assessed in the carbonated beverage sector by concentrating called "cloudy" and enzymatically liquefied liquid obtained by extraction of the mixture obtained after fragmentation. However, for this process, it is necessary to have a special substructure in factories. Since there is no infrastructure in some canned factory, all of the citrus peels go to waste and lead to environmental pollution (Güreş, 2014).

Antioxidants are, in a general sense, substances that protect the damaged cells by free radicals. Citrus peel residue is the primary waste by-product of the juice extraction industry. However, this peel is an interesting source of phenolic compounds, which include flavonoids. The concentrations of flavonoids in citrus fruit are highest in the peel Flavonoids have been found to have health-related properties, including anticancer, anti-inflammatory, cardio protective, and antioxidant effects (Rayeh et al., 2009; Ko et al., 2016).

Mandarin fruit has an important place in the citrus fruit family. The mandarin is one of the most popular fruits in different countries on the whole world. Fresh mandarin and peels of mandarin are rich in biologically active compounds such as antioxidants, flavonoids, vitamins, and other phenolic acids (Won et al., 2017). Mandarin is used in different areas due to its highly bioactive compounds. At the forefront of these fields are the food, agriculture and chemical industries. Besides these industries, today, studies on different uses of mandarin continue.

The aim of our study is to provide a healthy product to the people by combining the waste with the mandarin peels. Since the antioxidant activity in the mandarin peels, which is 100% natural, may be in the trash left in nature as waste; it is aimed to be used in the leather industry and converted into leather products that is organic and do not endanger to human health. It is planned that the products to be made in this way will be more resistant to sun and UV-rays.

Material and Method

Materials

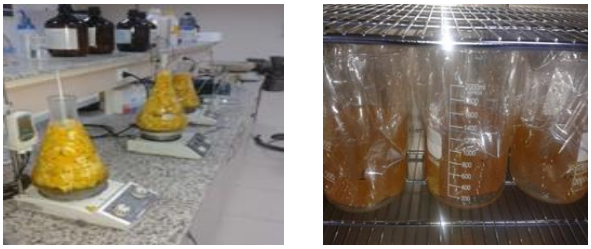
In the study, 9 pieces Turkish domestic goat skins were used. Every trials repeated four times. In first stage of study, waste mandarin peels were taken and brought to the laboratory. Waste mandarin peels have been held subject to extraction as mentioned in Bayramoglu et al. (2008). The mandarin peels were shown Figure 1.

Determination of Antioxidant Activity of Mandarin Peel Extract

Nowadays many methods have been developed for researching antioxidant capacity. Antioxidant assay methods include, DPPH (2, 2-diphenly-1-picrylhydrazly), Trolox antioxidant activity (TEAC), antioxidant power (FRAP) and Oxygen radical absorbance capacity (ORAC) analyses (Albayrak et al., 2010).

Mandarin peels have been extracted at a certain temperature and time. Thus, the water from the extract was evaporated. It was chosen at 60°C for extraction treatment. Extracted mandarin peels were demonstrated in Figure 2. (Bayramoğlu et al., 2008; Bayramoğlu et al., 2011). In the second part of the study, the inhibition capacity of DPPH radical of the extract produced from waste mandarin shells was determined by comparing the inhibition capacity of DPPH radical of Trolox, a synthetic vitamin E (Cemeroğlu, 2010). Trolox equivalent antioxidant capacity (TEAC) of the mandarin extract sample was determined as 65 GAE µM TE/g mandarin. This value shows that the antioxidant capacity on the DPPH radical of a 1 g sample of mandarin peel extract is equivalent to the antioxidant capacity with the 65 µM Trolox. In the third part of the research, leathers were processed according to a classical garment production prescription and the mandarin extracts were used after formic acid fixation at the final stage. In the study, control group (without any fixator) and commercial fixator were also used comparatively for control purposes.

Figure 1. Waste mandarin peel samples



(a) (b)

Figure 2. Extraction process of mandarin peels (a) and prepared extracts (b).

Processing of The Skin and Using of the Extract

In study, goat skin was processed according to a classical garment leather prescription and steps of the leather process were demonstrated at Table 1, Table 2 and Table 3.

Aging Process

The leathers have been aged in heat-adjustable UV cabinet (UV light of 254 nm) at 80 ° C temperature and under UV for 72h periods and ageing has also been implanted on all the other leather samples. Determination of the wet and dry rub fastness test was carried out on the Bally Finish Tester in accordance with EN ISO 11640 / IUF 450 /VESLİC C 4500 standard before and after ageing process.

Colour Measurement of Leather Samples

Colour measurements of the leathers were performed on a Konica Minolta CM-3600d brand spectrophotometer. L*, a* and b* values of leathers were recorded. The colour values of L* (brightness), a* (+ red, - green), b* (+ yellow, - blue) were determined. L* is a value ranging from 0 to 100. As the value of L* approaches 0, the colour of the product increases, while when it approaches 100, the brightness of the product increases. Results of colour values of leather samples were given at Table 4 and Table 5. ΔE value of leather samples were calculated according to equation below.

$$\Delta E = \sqrt{(L-L_0)^2+(a-a_0)^2+(b-b_0)^2}$$

Table 1. Prescriptions of the leather processed with mandarin extract

Treatment	%	Product	Temperature (°C)	Time (min)	pH
Drain-washing with cold water	150	Water	60	30 min	4
Horse up	2	Waste mandarin extract			

Table 2. Prescriptions of Control Groups

Treatment	%	Product	Temperature (°C)	Time (min)	pH
Drain-washing with cold water Horse up	300	Water	25	5 min	4

Table 3. Prescriptions of the leather treated with the fixator

Treatment	%	Product	Temperature (°C)	Time (min)	pH
Drain-washing with cold water	150	Water	60	30 min	4
Horse up	2	Fixator			

Table 4. Colour values calculated by Minolta before aging of leather

Fixators	*L**	*a**	*b**	ΔE
Control 1	18.99	-0.87	-0.79	-
Control 2	19.16	-0.71	-0.39	-
Control 3	20.12	-0.67	-0.54	-
Control 4	21.25	-0.64	-0.65	-
Mandarin 1	21.43	-0.09	-0.06	2.66
Mandarin 2	22.83	-0.12	-0.12	3.72
Mandarin 3	19.00	-0.50	-1.31	1.37
Mandarin 4	21.33	-0.51	-0.54	0.19
Fixator 1	21.57	21.57	-1.20	2.60
Fixator 2	21.15	21.15	-1.10	2.07
Fixator 3	20.78	20.78	-.0.99	0.73
Fixator 4	19.68	-1.01	-1.02	1.65

Statistical Evaluation

The statically differences between the data obtained in the study were calculated. SPSS 20.0 software program was used for evaluation experimental data. The multiple comparison test (Tukey test) in the SPSS program was used to evaluate the data. The differences between the results were evaluated according to the 95% confidence interval.

Results and Discussion

In the study, antioxidant activities of the mandarin peels extracts were examined. Antioxidant activity was determined using the DPPH method and antioxidant activity of mandarin extract was found 65 GAE µM TE/g. According to an investigation, at different temperatures, mandarin peels were dried. Temperatures were chosen as 60°C, 90°C and 120°C, respectively and the antioxidant activities of extracted and not extracted mandarin peels were compared. Antioxidant activity of not extracted mandarin peels was found higher than extracted mandarin peels as expected. There are many studies that antioxidants are sensitive to temperature. Due to the extraction temperature, the amount of antioxidants in extracted samples varies according to the raw material. In the same study, antioxidants result of fresh mandarin waste as found 161.04 µM TE/g and for extracted mandarin peels which are dried at 60°C, 90°C and 120°C, antioxidant results were found as 71.27, 106.38 and 140.82 respectively. It has been determined that the mandarin peels dried at high temperature have higher antioxidant activities after extraction (Martinez et al., 2016). In another study, antioxidant activity of 14 wild mandarin genotypes was investigated by using DPPH method. The DPPH values of the wild mandarins varied from 29.04 to 50.46l µM TE/g DM (Zhang et al., 2014). So, when we compere our study with the others, even different extraction and drying methods, it was seen that all mandarin peel extracts have antioxidant effect.

The leathers were processed according to a classical garment production prescription and the mandarin extracts were used after formic acid fixation at the final stage. Leathers were kept under 80°C/UV for 72 hours for aging process and the colour values of initial and hindermost leathers were measured with using of spectrophotometer. Colour values of the leathers before aging process were showed at Table 4. Every trials repeated four times so every group has four results. Colour values of the leathers after aging process were showed at Table 5.

The colour values of *L** (brightness), *a** (+ red, - green), *b** (+ yellow, - blue) were determined. L* is a value ranging from 0 to 100. *L** is a value ranging from 0 to 100. As the value of *L** approaches 0, the colour of the product increases, while when it approaches 100, the brightness of the product increases.

As a result of the study, when the results of mandarin extract and fixator were statistically evaluated by Tukey test, a significant difference was observed in the results ($P< 0.05$). According to results, the mandarin peel extract gave better results than the fixator. It is better against aging process. For this reason, it is thought that it can be used as a fixator.

Table 5. Colour values calculated by Minolta after aging of leather

Fixators	*L**	*a**	*b**	ΔE
Control 1	22.15	-0.86	-0.53	-
Control 2	21.78	-0.90	-0.46	-
Control 3	22.20	-0.93	-0.54	-
Control 4	27.31	0.13	1.90	-
Mandarin 1	24.99	-0.97	-0.36	2.84
Mandarin 2	23.27	-0.91	-0.49	1.49
Mandarin 3	24.93	-0.68	-0.26	0.38
Mandarin 4	24.93	-1.12	-0.30	3.48
Fixator 1	30.87	-0.18	1.71	9.02
Fixator 2	30.71	-0.55	1.92	9.25
Fixator 3	28.10	-0.66	1.05	6.11
Fixator 4	25.65	-0.68	0.98	2.06

The research findings clearly show that mandarin peels extract with antioxidant properties has been shown to reduce fading of leather colour as a result of leather aging. On the other hand, it is obvious that the fixator used turned on the colour and increased colour fade. Leather with antioxidant properties and increased light tolerance; it can be used comfortable and healthily in car making, clothes, shoes, bags and many others.

Conclusion

The use of antioxidants for leather aging is a new field of study. The main purpose of the study was to investigate the use of the mandarin peel extract as a fixator. When the mandarin peel was used as a fixator, the effect on the colour values of the skin sample was examined. There was a difference in colour values (bleaching) between the leather samples in which the mandarin peel extract was used as a fixator and the leather samples in which the mandarin peel was not used as a fixator. And this difference was found significant statistically ($P<0.05$). To demonstrate that the material has a very high rubbing fastness, samples with different rubbing values have been tested, up to 10 times higher than the standards. The success of the results opens up new investigations. The addition of different antioxidant substances and the use of different process parameters are considered to be successful results in this area.

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