Dyeing of Leather by Natural Bioactive Material

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Abstract: The presented research was designed to evaluate the use of natural material – cranberry pomace extract for chromed leather dyeing and to establish factors influencing on leather quality during the dyeing. The dyeing process influence on dyed and neutralised leather properties was explored. It was established that neutralisation process should be optimised seeking to improve the exploitation properties of finished leather. The increased amount of neutralising agent is necessary to improve bonding of fatliquors with dermal tissue. The application of dyeing with cranberry pomace extract and optimised neutralisation process leads to production of leather which properties meets the properties required for footwear leather.

***Keywords:** Leather, Cranberry pomace extract, Dyeing, Neutralisation.*

INTRODUCTION

Leather industry generates huge amount of various wastes which utilization is serious task for researchers. Waste from untanned, tanned or processed leather (mainly solid waste such as scraps, trimmings, dust, etc.) can be easily collected and some of this waste can be recycled into useful products [1-4]. Unfortunately, the removal of soluble wastes (mainly residuals of used for tanning chemical materials which are not fully taken up by leather and thus end up in tannery wastewater [5]) from wastewater is very complicated and expensive process. Leather industry consumes large amounts of chemicals – approximately 130 different types of chemicals [6] and the major variety of them uses for post-tanning processes. Chemical compounds such as deacidulants, synthetic and natural retanning agents, synthetic and natural oils, surfactants, dyes, chemical auxiliaries, and acids are added during the post-tanning process to ensure the desired properties to the leather [5].

Dyes have a particular variety because of the large number of colours and shades that need to be obtained. Accordingly can be used the dyestuffs of various chemical composition: direct, reactive, acid etc. or even their mixtures. This fact complicates the wastewater cleaning from residuals of synthetic dyes. The proposed methods to achieve this objective are quite complex. R.H. Senay et al. [7] suggest using metal-chelated spherical particulated membranes for removing acid dye from leather wastewater. Xu et al. [8] developed a multifunctional gelatine–quaternary ammonium copolymer as an efficient material for reducing dye emission in leather tanning process.

Probably the simplest way to solve the problem of pollution by synthetic dyes used for leather colouring is to refuse from them and apply natural colouring materials. For example, brown colour of leather can be obtained using natural vegetable tannins such as mimosa, quebracho, pine, acacia because mostly of vegetable tannins has brown colour. Of course, shades of brown colour differ and depend on the tannin used. The attempts to use other natural colorants for leather to get other than brown colours are carrying out.

Study of Velmurugan et al. evaluated the extraction of two colors of dye (yellow and brown) from *Coreopsis tinctoria* flower petals using ultrasound and the dyeing of leather with the extracted dyes as a source of nontoxic and eco-friendly dye [9]. Leather dyeing was optimized with the aid of ultrasound and magnetic stirring.

Biocolorant obtained from *Monascus purpureus*, which yields red colored extract, has been studied for the dyeing process of leather [10]. The effect of varying conditions like pH, concentration, time and temperature on the levelness of the dyeing, shade brightness, color intensity and exhaustion of the dye have been studied herein, and the conditions optimized. The bulk properties viz., softness and grain smoothness have been found to be marginally improved, versus control, in biocolorant treated leathers.

Kurinjimalar et al. report about exploiting madder root dye (*Rubia cordifolia L.*) for leather dyeing application [11]. The ground madder yields a deep yellow-based red colour. At optimum dyeing parameters, it shows good fastness, perspiration, organoleptic properties without affecting the physical characteristic.

Unfortunately, the main disadvantage of these natural dyes lies in the order of magnitude of their extraction yield factors (a few grams of pigment per kg of dried raw material). This makes their current market price about USD 1/g, thus limiting their application to high-value-added natural coloured garments [12].

The price of biocolorant can be reduced when it is produced not directly from plants, fruits or berries, but from the waste from their processing.

In the Department of Food Science and Technology of Kaunas University of Technology (Lithuania) a water extract was prepared from defatted cranberry pomace by pressurized liquid extraction [13]. The obtained dry cranberry pomace extract (CPE) contained comparatively high amount of proanthocyanidins (14.79 mg/g) and was characterized as having strong antioxidant properties and intense red colour.

Therefore, the main aim of the research was to apply the cranberry pomace extract (CPE) obtained by pressurized liquid extraction as a bio-dye for chromed leather.

MATERIALS AND METHODS

Materials

Chromed semi-finished leather (purhased from JSC „TFL Oda", Lithuania) was used as raw material for this study (Figure 1, A).

Dry cranberry pomace extract obtained by pressurized liquid extraction (Department of Food Science and Technology of Kaunas University of Technology, Lithuania) was used for chromed leather dyeing (Figure 1, B). The main characteristics of the wet-blue leather and the CPE are presented in Table I.

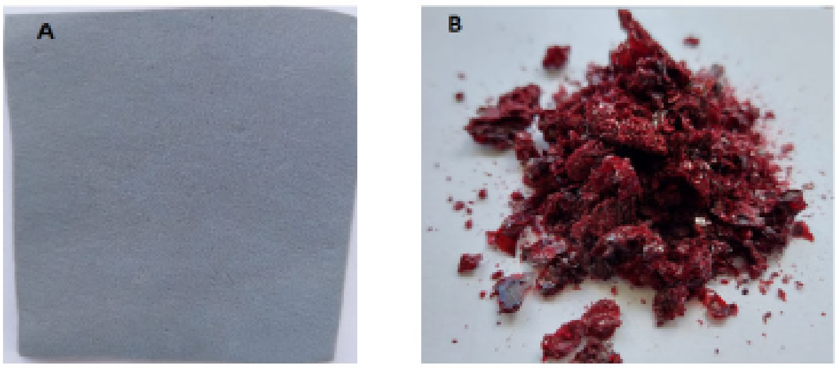

Fig. 1. Chromed semi-finished leather (wet blue) (**A**) and cranberry pomace extract (**B**).

TABLE I. MAIN CHARACTERISTICS OF SEMI-FINISHED LEATHER AND CRANBERRY POMACE EXTRACT

Object	Index	Value
Chromed semi-finished leather	thickness, mm	1.4-1.6
	shrinkage temperature, °C	110.3
	amount of Cr_2O_3, %	4.09
	pH	2.97
Cranberry pomace extract	moisture content, %	5.83
	pH (10 % solution)	2.94
	pH (2 % solution)	2.95
	pH (1 % solution)	2.98

The chemicals used for the analysis were of analytical grade. The analytical and technical grade materials were used for the technological processes (fatliqours Oleal 146, Oleal 1946, Fospholiker 661 and Fospholiker 6146 produced by *Codyeco* S.p.a. (Italy) were used for fatliquoring of leather).

Technological processes

The technological processes were carried out as follows (percent based on chromed leather weight):

Washing: water 100%, temperature 30-32 °C, 0.5 hour. Drain.

Dyeing: H_2O 150 %, temperature 30-32°C, CPE 2, 6 or 10%, duration 1.5 hour. Drain.

Neutralisation: H_2O 150 %, temperature 30°C, $NaHCO_3$ 1.5 %, duration 30 min; HCOONa 2 %, duration 1.5 hour. Drain.

Washing: water 100%, temperature 50-52 °C, 0.5 hour. Drain.

Fatliquoring: water 200%; temperature 58-62 °C; Oleal 146 2%; Oleal 1946 4%; Fospholiker 661 3%; Fospholiker 6146 4%; 1 hour; HCOOH 0.5%; 20 minutes; HCOOH 0.5%; 20 minutes. Drain.

Washing: water 100%; temperature 30 °C; 0.5 hour. Drain.

Drying: the samples were placed on a table and dried in a free state for 48 hours at 22-25 °C.

Analysis Methods

The shrinkage temperature of the chromed leather samples was determined as described in the literature using special equipment and replacing the distilled water with glycerol [14].

The penetration of dyes through hide tissue was observed using the special optical microscope with scale (magnification 15 times) MPB-2 (Russia).

The strength properties, the amount of chrome compounds in the leather, matter soluble in dichloromethane, and volatile matter were determined according to the standards [15-18].

The pH of solutions was directly measured using pH-meter pH 526 (WTW, Lenkija); the pH of leather was determined according to standard [19] using the same pH-meter.

RESULTS AND DISCUSION

According to the conventional technology of leather processing commonly leather is dyeing after neutralization process when pH of leather is about 5-7. Such pH of leather is appropriate for qualitative penetration of synthetic dyes and fatliquoring materials. Unfortunately, the CPE at the same pH becomes insoluble and unsuitable for treatment of leather. Therefore, it was the main reason why dyeing with CPE was carried out before neutralisation. At the same time, the CPE behaves like indicator when the pH of medium changes: CPE turns grey-green when the pH of the medium reaches 4-4.5. The dye penetration dependence on the amount of CPE was observed using optical microscope (Figure 2). The indexes of dyeing process and subsequent neutralization were determined and assessed (Table II).

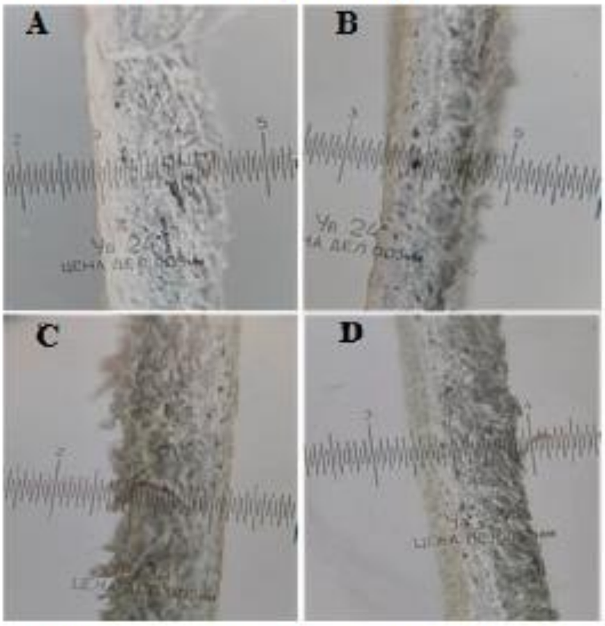

Fig. 2. Dyed with CPE and neutralized samples (**A** – control (not dyed); **B** – 2 % CPE; **C** – 6 %; **D** – 10 %).

The results of dye penetration measurement (Figure 2) allow conclusion that for qualitative "surface dyeing" 6-10 % of CPE are necessary to employ.

TABLE II. EFFECT OF DYEING WITH CPE ON DYED AND NEUTRALISED LEATHER PROPERTIES

Index	CPE, %			
	2	6	10	not dyed (control)
After dyeing:				-
pH of solution	2.99	2.67	2.55	-
pH of leather	2.76	2.65	2.60	-
Shrinkage temperature, °C	110.7	108.3	104.3	-
After neutralization				
pH of solution	7.39	5.92	5.50	7.12
pH of leather	4.63	4.02	4.05	4.72
Shrinkage temperature, °C	115.3	113.7	111.4	116.5

It is seen (Table II) that higher amount of CPE when dyeing leads to more significant lowering of leather shrinkage temperature. During neutralisation, the shrinkage temperature rises and even exceeds the shrinkage temperature of "wet blue" leather. Again, the highest shrinkage temperature is of the sample dyed with the lowest amount of CPE.

On the other hand, the pH of leather dyed using 6 or 10 % of CPE after the neutralization is too low for qualitative fatliquoring process. Accordingly, seeking to reach the pH of the dyed using 10 % of CPE leather not less than not dyed but neutralised leather, neutralization was repeated for so dyed leather increasing amounts of neutralising materials and carried out accordingly: H_2O 150 %, temperature 30°C, total duration 1.5 hour; 1st variant – $NaHCO_3$ 2 %, duration 30 min; HCOONa 2 % duration 1.5 hour; 2nd – $NaHCO_3$ 3 %, duration 30 min; HCOONa 3 %, duration 1.5 hour, and 3rd – $NaHCO_3$ 3 %, duration 30 min; HCOONa 6 %, duration 1.5 hour. The results are presented in Table III.

TABLE III. INFLUENCE OF NEUTRALIZATION CONDITIONS ON THE PROCESS AND LEATHER PROPERTIES

Index after neutralization	Variant of neutralization		
	1st – $NaHCO_3$ 2 %, HCOONa 2 %	2nd – $NaHCO_3$ 3 %, HCOONa 3 %	3rd – $NaHCO_3$ 3 %, HCOONa 6 %
pH of solution	5.33	6.89	7.10
pH of leather	4.44	5.21	5.26
Shrinkage temperature, °C	114.8	115.0	114.0

Considering the achieved leather pH and the material consumption, 2nd variant of the neutralizations was chosen as optimal option for this case.

For the final evaluation of the dyeing using CPE and subsequent neutralisation according to the chosen methodology, leather was fatliquored, dried (Figure 3) and its chemical and strength properties determined. The main indexes of the obtained leather are presented in Table IV.

Fig. 3. Dyed with CPE and finished leather.

TABLE IV. PROPERTIES OF FINISHED LEATHER OBTAINED AFTER DYEING WITH CPE

Index	Experimental	Control
Amount of matter soluble in dichloromethane, %	9.1	12.1
Shrinkage temperature, °C	110.7	109.0
Amount of Cr_2O_3 in leather, %	3.61	3.74
Tensile strength of leather, N/mm^2	16.2	15.5
Grain strength, N/mm^2	16.2	15.5
Relative elongation at break at the strain 10 N/mm^2, %	31.4	45.7
Relative elongation at break, %	59.2	67.8

There are two main points were the properties are different: the experimental leather was characterised by less amount of matter soluble in dichloromethane and less relative elongation. By the way, the second index can be dependent on the first. On the other hand, both leathers meet the quality requirements for shoe upper leathers.

CONCLUSION

CPE can be used to dye the chromed semi-finished leather. When applied to 10 % of the weight of the semi-finished product, the CPE penetrates sufficiently to meet the requirements of a surface dyed leather. On the other hand, with this amount of CPE, the pH of the skin is low and more neutralizing agents are needed to neutralize it. After the wet finishing processes and drying, the resulting leather meets the properties required for footwear leather.

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