Industrial Crops and Products 53 (2014) 16–22

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Optimization of tannin isolation from acorn and application in leather processing

Ersin Onem[a], Gurbuz Gulumser[a], Seref Akay[b], Ozlem Yesil-Celiktas[b,*]

[a] Department of Leather Engineering, Faculty of Engineering, Ege University, Bornova-Izmir, Turkey
[b] Department of Bioengineering, Faculty of Engineering, Ege University, Bornova-Izmir, Turkey

ARTICLE INFO

Article history:
Received 10 October 2013
Received in revised form 5 December 2013
Accepted 9 December 2013

Keywords:
Leather
Acorn
Valonea tannin
Optimization
Box–Behnken design
Tanning

ABSTRACT

The aim of this work was to optimize the extraction parameters of tannins from the acorns and the tanning properties. Experiments were planned to evaluate the effect of solvent/feed ratio (20–100 ml/g), time (2–10 h) and solvent mixture ratio (methanol–water) (0–100%) on extraction yields, tannin contents and total tannin amounts. Valonea tannin obtained under optimum conditions was applied to leather tanning process where filling coefficient (%) and shrinkage temperature (T_s) of the leathers were examined. Optimum extraction parameters were elicited as 100 ml/g for solvent/feed ratio, 6 h of process duration and solvent mixture ratio of 62% methanol–38% water. The filling coefficient of the leathers tanned with extracted valonea (57.81%) and the shrinkage temperature (75.5 °C) was superior to the commercial valonea (52.83%, 73 °C) implying the significant impact of process optimization. The tanning properties of the extracted valonea were satisfactory for the vegetable tanning in leather industry.

1. Introduction

Leather production is an ancient technology that has been described as man's first manufacturing process. It comprises the transformation of raw putrescible animal hide/skin into useful materials (Thomson, 2006; Falcão and Araújo, 2011). After pelting, hides and skins are susceptible to attack by bacteria and microorganisms. The collagen structure of the hide/skin must be stabilized by means of the tanning process to avoid its degradation. Of all the existing tanning processes, chrome tannage is the most widely used technique by the leather industry worldwide. Approximately 90% of the tanning process is carried out with chromium (Cr) (III) salts (Sundar et al., 2002; Marsal et al., 2012).

The traditional chromium tannage process with chromium salts is highly pollutant (Pansera et al., 2004). Likewise, Cr (III) in leather may also oxidize into Cr (VI) because of the aging of leather products with time due to the influence of various environmental conditions such as heat, light, and humidity. Chromium tanning and auxiliary agents replace molecules of the leather structure and free radicals are subsequently formed during the degradation process which occurs due to the effects of temperature and UV lights. As a result of these radicals, there is a potential tendency for Cr (III) to oxidize to Cr (VI) (Puntener, 1996; Bayramoglu et al., 2012). Human health is seriously impaired as Cr (VI) occurring in leather products oxidize to Cr (III). The use of natural compounds in the leather manufacture has become extremely important with the increase of environmental awareness and interest in the ecological leather products. (Sundar et al., 2013; Bayramoglu et al., 2011; Onem et al., 2011; Bayramoglu et al., 2012). The use of plant polyphenols has come into prominence in tanning which is the most important process of leather manufacturing (Kanth et al., 2009).

Tannins are complex and heterogeneous group of polyphenolic secondary metabolites of higher plants with molecular weights between 500 and 20,000 Da and soluble in water and polar organic solvents (Haslam, 1996) sharing the ability to bind to and precipitate proteins, alkaloids and polysaccharides. Vegetable tannins are generally divided into hydrolyzable and condensed ones and are found in roots, flowers, leaves and woody parts of many plants (Claudio et al., 2011). Although almost all plants contain tannins, only few species have sufficient amounts to be of commercial importance. Many of the commercially most significant tannin materials originate in tropical or sub-tropical climes (Haslam, 1989; Kilicariaslan and Ozgunay, 2012).

Valonea, which is the hydrolyzable tannin obtained from the fruits of acorn growing naturally in the west part of Turkey, has a significant economic value for the leather industry. It has been long commercially used to extract ellagitannins as tanning agent, a low added value product about 500$ per ton, which convert hides/skins into leather (Britta et al., 2002; Huang et al., 2008). Valonea tannin

* Corresponding author. Tel.: +90 232 3434400; fax: +90 232 374 42 89.
E-mail addresses: ozlem.yesil.celiktas@ege.edu.tr, ozlemyesil@gmail.com (O. Yesil-Celiktas).

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http://dx.doi.org/10.1016/j.indcrop.2013.12.014

Table 1
Recipe for the production of leathers.

Process	Amount (%)	Chemicals	Temperature (°C)	Time (min)	Remarks
Depickle	250	Water 6–7 Be	30	20	
	1.5	Sodium formate		30	
	4	Degreasing agent		30	
	1	Acidic enzymatic bating agent		60	
	0.5	Sodium bicarbonate		90	pH 4.5–5.0-Drain
Washing	150	Water	30		
	0.5	Tensid		20	Drain
Washing	150	Water	30		
	0.5	Tensid		20	Drain
Tanning	200	Water	30		
	2	Naphthalene syntan		20	
	5	Tannin		30	
	1	Synthetic fatliquor agent with emulsifier		20	
	4	Tannin		30	
	1	Synthetic fatliquor agent with emulsifier		20	
	4	Tannin		30	
	1	Synthetic fatliquor agent with emulsifier		300	
	x	Formic acid		60	pH 3.5–3.6
Washing	200	Water		10	
Horsing					

is obtained from the cups and beards of acorns by conventional hot water extraction. It mostly finds application in the natural tannage of leather, as an alternative procedure to chromium tannage and one of the well-known vegetable tannin used for retannage processes in leather production.

The extraction process of tannins from natural matrix is currently performed by empirical methods where no process optimization has been carried out (Guerrero et al., 2008; Claudio et al., 2011) and is influenced by the chemical nature of the tannins, employed extraction method, particle size of the plant material, storage time and extraction conditions. Amount of solvent, temperature and processing time have great influence on extraction yield, concentration and tannin content of the extract which in turn influences the quality of tannin (Naczk and Shahidi, 2004). Therefore, optimization of extraction conditions is of prime importance for scale up of the process for the ultimate aim of commercialization.

In this study, solvent extraction of valonea tannin from the acorn cups and beards was carried out and optimization of the extraction parameters was investigated with Box–Behnken experimental design (BBD). Tanning properties of the extract were also investigated in terms of filling coefficient, and shrinkage temperature of the leathers tanned with valonea tannin obtained under optimum conditions and compared to that of the commercial valonea tannin.

2. Materials and methods

2.1. Materials

Cups and beards of acorns used for the extraction processes were obtained from Balaban Izmir Palamut Ltd. Company operating in Manisa/Turkey. Commercial valonea tannin was donated from Sepiciler Leather Company. Low-chromed (Cr_2O_3 content < 0.8%) hide powder used for the determination of tannin content of the extracts was purchased from FILK (Research Institute of Leather and Plastic Sheeting), Freiberg, Germany. Domestic pickled sheep skins were used in the tanning process. Methanol was from Merck and all other chemicals were of analytical-grade purity. Nanopure water used in the analysis was prepared by using in-house nanopure water system (Sartorius Arium 611, Sartorius-Stedim, Goettingen, Germany).

2.2. Determination of moisture content of acorns

Moisture content of the acorns was determined according to SLC 113 standard method (SLC-113, 1996). The experiments were done in triplicate and average moisture content was determined.

Table 2
Experimental design for solvent extraction of the beards of acorns.

Samples	Factor 1 A: solvent/feed (ml/g)	Factor 2 B: time (h)	Factor 3 C: solvent mixture (%)	Response 1 Extraction yield (%)	Response 2 Insoluble solids (%)	Response 3 Total dissolved solids (%)	Response 4 Non-tannins (%)	Response 5 Tannin content (%)	Main response Tannin amount (g) (Beards of 100 g)
SE1	100.00	8.00	0.00	55.92	3.49	96.51	34.46	62.05	34.70
SE2	100.00	8.00	100.00	51.05	4.93	95.07	27.93	67.14	34.27
SE3	60.00	6.00	0.00	53.27	2.09	97.91	33.57	64.34	34.27
SE4	60.00	8.00	50.00	57.65	4.50	95.50	30.87	64.63	37.26
SE5	100.00	6.00	50.00	66.27	4.88	95.12	26.82	68.30	45.26
SE6	20.00	10.00	50.00	51.56	5.27	94.73	28.55	66.18	34.12
SE7	100.00	10.00	50.00	48.10	3.87	96.13	29.15	66.98	32.22
SE8	20.00	6.00	50.00	47.68	2.85	97.15	30.23	66.92	31.91
SE9	60.00	8.00	50.00	59.10	6.59	93.41	28.41	65.00	38.42
SE10	20.00	8.00	0.00	43.21	8.10	91.90	29.89	62.01	26.79
SE11	20.00	8.00	100.00	44.83	2.78	97.22	29.81	67.41	30.22
SE12	60.00	10.00	0.00	45.29	1.67	98.33	32.69	65.64	29.73
SE13	60.00	8.00	50.00	57.55	2.43	97.57	28.88	68.68	39.53
SE14	60.00	6.00	100.00	46.48	2.92	97.08	29.88	67.20	31.23
SE15	60.00	10.00	100.00	51.65	3.40	96.60	28.33	68.27	35.26

Factor 3; 0: 100% H_2O, 50: 50% MeOH + 50% H_2O, 100: 100% MeOH.