INT. J. BIOL. BIOTECH., 10 (1): 29-35, 2013.

QUANTIFICATION OF PHYSICAL TESTING OF LEATHER THROUGH APPLICATION OF DIFFERENT RETANNING PRODUCTS

Beena Zehra*,[1,2], Syed Shahid Shaukat [1] and Omm-e-Hany [1]

[1]*Institute of Environmental Studies, University of Karachi, Karachi 75270, Pakistan.*
[2]*Leather Research Centre, PCSIR, D-102 , South Avenue , SITE, Karachi, Pakistan.*
(*Corresspondance at : zehrabeena@yahoo.com)

ABSTRACT

Two retanning products were prepared by utilizing waste protein of chromium containing solid wastes. One retanning product was prepared by alkaline protein hydrolyzate while the other was prepared by acidic protein extracted from chromium containing solid wastes (chrome shavings). Whereas two retanning products were commercial and applied in the same dosage in goat skin processing for comparison of results. The impact of four different leather retanning products was evaluated by analyzing data from standard physical testing of leather. ANOVA and Duncan's multiple range tests were employed to compare the physical testing methods. Results revealed that retanning product prepared from the recovered protein was effective as a retanning product. The results of ANOVA for various parameters such as tensile strength (N/mm^2), tear strength (N/mm), etc. were found significant (p at the most 0.05).

Key-words: Retanning products, Leather, Proteins, Amino acids, Chromium trivalent, Chromium hexavalent

INTRODUCTION

The usual way for handling of chromium containing solid wastes generated from tanneries in most of the countries is land filling, throwing at dumping sites and incineration(Taylor *et al*., 1998). These wastes mainly consist of collagen and chromium III complexes which could be treated to give the potential resources of collagen protein and the chromium compounds (Heidmann 1991). Chromium containing solid wastes may be managed through more sustainable technological protocols such as hydrolysis of shavings with alkalis such as CaO, NaOH and MgO at moderate temperatures (Taylor *et al*., 1998 ; Holloway 1978; Batille *et al*., 1983; Guardini 1990; Reis and Beleza 1991; Mu *et al*., 2003; Tahiri *et al*., 2006; Langmaier *et al*., 2006) and oxidative de-chroming (Sun *et al*., 2003 ; Cot *et al*., 2003) have been studied to recycle amino acids and peptides usable for animal feeds, fertilizers, packaging for agriculture. Chromium containing solid wastes have various applications in different products such as feed additives (Cabeza *et al*., 1998) fertilizers (Taylor *et al*., 2004) and chemicals (Santos and Gutteres , 2007) while chromium solid free wastes are used for the production of gelatin and collagen hydrolyzates (Morimura *et al*., 2002). Although, these solid wastes carry a high potential of reutilization in many industries but disposition and storage of these contaminated material is very costly and environmentally undesirable in many places. Therefore, the reutilization of chromium containing solid wastes is encouraged to develop the cleaner leather technology. Therefore, leather retanning products through recycling require urgent investigations for the leather processing to replace or minimize the pollution load caused by commercial organic synthetic retanning agents such as phenols, aldehydes, etc. With these consideration in mind, in this study hydrolyzed waste protein of chrome shavings is utilized for the preparation of retanning agents using different chemicals and simple methods. These retanning products have been applied in leather processing and then characterized through physical properties of resulted leathers.

MATERIAL AND METHODS

Chromium containing solid wastes commonly called chrome shavings were collected from tannery area of Leather Research Centre, PCSIR (SITE area) from processing. These are small pieces of leather that are collected when the thickness of wet blue is becoming uniform by a shaving machine. These chrome shavings were analyzed for moisture content, pH, ash and chromium oxide (Table 1) then kept at room temperature till used for experimental work.

Moisture content in chrome shavings was carried out according to SLC 3 (IUC 5), pH by (ASTM, D,1293-99), ash by (ASTM, D, 2617-96: SLC 6, IUC-7), fat by ISO 4048: 1977), chromium oxide by SLC 22, IUC 18,EN 420, amino acid profile by (AOAC, 2005). While for physical testing sample cutting by (BS-3144 IUP-1/EN ISO 2419: 2006), conditioning of leather (SLP3, IUP 3; BS 3144: method 2, 2001), thickness by SLP4 , IUP4; BS 3144: method 3), tensile strength and elongation at break by (BS-3144, IUP-6/EN ISO 3376: 2002), distension and

strength of grain by ball burst (SLP 9, IUP /9;BS3144: method 8). Universal Testing Machine from Tinius Olsen was used for physical testing of prepared leathers.

Statistical analysis

Data from physical testing parameters of all four leather products was subjected to analysis of variance (ANOVA). Duncan's Multiple Range Test (DMRT) was also used to compare the means of all four treatments (Zar, 1999).

Chromium containing solid wastes (chrome shavings) were washed thoroughly with water to remove any dust particles then it was hydrolyzed in autoclave using 6% magnesium oxide and water was added as hydrolyzing medium and mixed thoroughly. Then, hydrolysis was carried out in autoclave for continuous 3 h at 95^0C to liquefy completely. Subsequently, hydrolyzed protein was filtered through fine muslin cloth and stored in refrigerator (4^0 C) till used for experimental work. While residue solid chrome cake was separated after filtration and it was used to prepare tanning agent. Percentage of amino acids was determined in crude protein (mg/gram), percentage of amino acids in crude protein (%), and amino acids in dry matter on misture free basis (Table 2).

Treatment - 1

In a three neck reaction flask 100g starch was taken in 600ml of distilled water at a temerature of 80^0C until a clear solution of starch was obtained. Thereafter, 100 g of protein (on moisture free basis) isolated from chrome shavings was added and stirrered for 10 minutes. Subsequentely, 40% acrylamide solution in distilled water based on isolated protein weight was also added with stirring at the same temperature. Then 10 ml (35%) hydrogen peroxide solution was also added with the addition of acrylamide whereas on the other neck of the flask 25g of sodium metabisulphite was added to the reactor over a period of 30 minutes. Reaction was allowed to proceed for 2 h heated at 75-80 ^{0}C with stirring while mouth of the reaction flask was covered after addition. Initially, the color of reactants was slightly whitish while after completion of 2 h, the polymeric solution was viscous and dark brown. The resultant polymeric retanning product devoid of monomer smell was cooled at room temperature and transfered into other flask. The pH of resultant product was 4.0 which was increased by sodium hydroxide solution to 5.0-5.5 with strirring while addition.

Treatment-2

Chrome shavings (100 g) was weighed and hydrolyzed with 3.259 mol/L of formic Acid in distilled water at 90^0C in autoclave for contineous 3h. After completion, the hydrolyzate was transferred into a beaker, cooled at room temperature. The pH of the hydrolyzate was 3.0 adjusted to 6.0 with 4.345 mol/L of sodium hydroxide solution in water and allowed to settle down for overnight at room temperature. After 24 h, hydrolyzate was centrifuged at 4500rpm for 10 minutes then supernatant was separated carefully and remaining solid residue was discarded. A dark green colored hydrolyzate was prepared after hydrolyzing of chrome shavings. The prepared chrome shaving hydrolyzate taken in a round bottom flask fitted with circulation reflux, reacted with stated amount of acrylamide (40% based on chrome shaving hydrolyzate volume) at 70 – 80^oC with continuous stirring for 2 h while 1.5% of hydrogen peroxide was also added drop by drop in a reaction flask during reaction. The reactants were cooled at room temperature. Finally, yellow colored reaction product was obtained with a pH of 6.5.

Treatment 3-4

Two commercial retanning products were applied in the same dosage. These were ART -1 and MK from BASF for comparison of results.

Application of Retanning Products

A goat skin was processed upto wet blue by normal chrome tanning process. After preparation, wet blue was kept for 3-4 days at room temperature for ageing then shaved at 1.0mm for smooth thickness. It was cut into four pieces and each piece was processed separately while all retanning products were applied in the same dosage. Each piece of wet blue was processed separately as described below.

Mechanical Operations at tannery

Washing

Wet blue was washed with water at 35^oC (300%) to remove any dust particles then drumming was carried out for 10 minutes.

Neutralization

Wet blue was neutralized with water (100%), sodium bicarbonate (0.8%), sodium formate (1.0%) then drumming was carried out for 60 minutes. The pH of wet blue was 6.5. After 24 h, float of drum was drained and washed twice with water (300%).

Retanning

Wet blue was retanned with water at 50^0C (150%) and prepared retanning product (10%) and drumming was carried out for 60 minutes. Then formic Acid (0.25%) was added and drumming was carried out for further 20 minutes. The float of drum was drained and washed with water (200%) with a final pH of 4.6.

Fatliquoring

Wet blue was fatliquored with water at 65^oC (200%) with 6% SR Synthetic Fatliquor and 6% UPN Fish Oil. Then, drumming was carried out for 120 minutes continuously. Formic acid (0.5%) diluted with 10ml of water was added and drumming was carried out for 30 minutes. The pH of leather was adjusted at 3.8 after complete fatliquoring process.

Drying

Leather was washed with excess of water and horsed up overnight approximately 12h then set out at room temperature. All chemicals used in the mechanical operations were given based on shaved weight of each wet blue piece.

RESULTS AND DISCUSSION

In the first step collection of chrome shavings, analysis and then basic hydrolysis of chrome shavings was carried out for the recovery of protein. In the second step retanning products were prepared and applied. The results in Table 1 show moisture content (%), ash (%), chromium oxide (%) and pH. These values were found very similar to those reported in literature (Jianzhong *et al*., 2004).

Subsequently, hydrolysis of chrome shavings was carried out and two fractions were isolated after complete hydrolysis of chrome shavings these were liquid protein and solid chromium sulfate as residue. Recovered protein hydrolyzate was tested for amino acids content as decribed in Table 2. Dry matter was found 92.2% and crude protein was found 69.7% containing different amino acids.

The alkaline hydrolysis of chromium containing leather wastes generates a chromium rich solid residue known as chrome cake in which residue proteins are crosslinked with chromium remaining as a by-product in the hydrolysis processes (Cabeza *et al.,* 1998c) and a liquid hydrolyzed protein (Gutterres and Silva, 2010 ; Crispim, and Mota, 2003; Tahiri *et al*., 2004) The results presented in Table 2 show that protein isolated from chrome shavings has different percentages of different types of amino acids. The collagen protein of chromium containing leather waste once separated after removing chromium have potential use as a leather tanning or finishing agent (Manzo and Fedele ,1994 and 1996). The advancement of leather for the loose areas and for the poor grain break are mainly value added issues in tanneries. The possibility for using cheap sources of protein as a raw material for the preparation of retanning agents is an interesting current issue and has shown effective results (Balada *et al*., 2009). Protein based fillers play a valueable role for the prodction of good quality leather because these types of fillers required some chemical reaction, moreover, the fixation of these protein fillers is not directly propotional to the available fibre structure (Spier, 2005). Retanning of leather fills the looser areas of hides and skins and improves the leather properties such as softness, fullness grain smoothness, etc. Due to multifunctional properties, leather protein is suitable for use as a component of polymer complex to improve the flexibility and firmness of leather. The results from Duncan's multiple range test (DMR test) are summarized in Table 3. The results of ANOVA for various parameters are given in Tables 4(a-g). All seven test parameters were found to be significant (p at the most 0.05). Graft copolymerization of starch with vinyl monomers was expected in the presence of oxidizer (Shenghua *et al*., 2005). While the reaction of amino acids has been studied to be esterification by starch (Kapusnaik *et al*., 1999). Furthermore, the graft modification of some amino acids of hydrolyzate protein may also occur with vinyl monomers as reported earlier (Jianzhong *et al*., 2004). Although, the retanning product from treatment 2 was the most effective for increasing the tensile strength (N/mm^2) as compared to other three treatments. However, the acidic hydrolysis of chrome shavings is not a safe method due to the oxidation of Cr trivalent into Cr hexavalent form having greater toxicity and carcinogenecty (Shapcott and Hubert, 1979). Therefore, it is suggested that retanning product from alkaline hydrolysis treatment is a good alternative for the retanning (Gutterres and Silva, 2010). The chemical composition of chrome shavings makes them suitable for processing to recover their constituents but the economics of the process is very important for industrial implementation (Cabeza *et al*., 1999).

Table 1. Analysis of Chrome shavings.

Test Name	Results
Moisture Content	7(%)
pH	3.8
Ash	11.5(%)
Chromium Oxide	3.5(%)

Table 2. Amino acid Profile of extracted protein from leather wastes.

Amino acids	Content (%)	AA in CP (%)	Amino Acid in CP (mg/g)	AA in DM (%)
Aspartic Acid	6.44	9.24	92	6.98
Threonine	1.44	2.07	21	1.56
Serine	0.50	0.72	7	0.54
Glutamic Acid	6.37	9.14	91	6.91
Proline	11.88	17.04	170	12.89
Glycine	15.09	21.64	216	16.37
Alanine	0.65	0.93	9	0.70
Cystine	0.58	0.83	8	0.63
Valine	1.23	1.76	18	1.33
Methionine	0.36	0.52	5	0.39
Isoleucine	0.74	1.06	11	0.80
Leucine	2.53	3.63	36	2.74
Tyrosine	0.73	1.05	10	0.79
Phenylaline	1.20	1.72	17	1.30
Histidine	0.38	0.55	5	0.41
Lysine	2.24	3.21	32	2.43
Arginine	3.80	5.45	55	4.12

Dry Matter 92.2%, Crude protein 69.7%; AA= Amino Acid, CP = Crude Protein, DM = Dry Matter

Table 3. Physical Testing Results of Retanning Treatments (01-04).

Treatment	Thickness (mm)	Tensile Load (N)	Elongation (%)	Tensile Strength (N/mm^2)	Tear Strength (N/mm)	Distension at break (mm)	Bursting Load (N)
01	1.566 a	347.221ab	131.816b	22.157b	86.314a	45.206bc	336.336b
02	1.343ab	447.055a	174.330a	33.244a	67.272b	32.046c	723.495a
03	1.000c	203.555b	83.616c	20.355b	36.841c	52.258ab	375.611b
04	1.186 bc	294.111b	101.696c	23.860b	23.547c	65.613a	312.939b
LSD (0.05)	0.228	138.444	28.857	8.098	14.101	19.098	79.184

DMR test (0.05), Means followed by the same letters are not significantly different from each other.

Table 4(a). One Way ANOVA Completely Randomized for Thickness (mm) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	0.519	3	0.173	11.720	0.01
Error	0.11	8	0.014		
Total	**0.637**	**11**			

Table 4(b). One Way ANOVA Completely Randomized for Tensile Load (N) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	93234.050	3	31078.016	5.748	0.05
Error	4352.722	8	5406.590		
Total	**136486.772**	**11**			

Table 4(c). One Way ANOVA Completely Randomized for Elongation (%) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	1415.9257	3	4717.308	20.082	0.001
Error	1879.173	8	234.896		
Total	**16031.098**	**11**			

Table 4(d). One Way ANOVA Completely Randomized for Tensile Strength (N/mm^2) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	296.638	3	98.879	5.344	0.05
Error	148.005	8	18.500		
Total	**444.643**	**11**			

Table 4(e). One Way ANOVA Completely Randomized for Tear Strength (N/mm) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	7323.411	3	2441.137	43.522	0.001
Error	448.708	8	56.088		
Total	**7772.119**	**11**			

Table 4(f). One Way ANOVA Completely Randomized for Bursting Load (N) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	334116.495	3	111372.165	62.986	0.001
Error	14149.505	8	1768.688		
Total	**348266.000**	**11**			

Table 4(g). One Way ANOVA Completely Randomized for Distension at break (mm) of Leather Samples.

Source	SS	df	MS	F	P
Main Effects St	1764.706	3	588.235	5.717	0.05
Error	823.088	8	102.886		
Total	**2587.794**	**11**			

REFERENCES

Balada, E.H., M.M. Taylor M.M, E.M. Brown and C.K. Liu (2009). Whey Protein Isolate, A potential filler for leather Industry. *Journal of American Leather Chemists Association.*, 104: 122-129.

Batille, P , F. Gagnon and W.E. Smith (1983). Upgrading leather and felt scrap into proteins , *Journal of American Leather Chemists Association* 78: 328-337.

Cabeza, L.F., A. J.Mcaloon and W.C Yee.(1998a). Process simulation and cost estimation of treatment of chromium containing leather waste *Journal of American Leather Chemists Association.*, 93: 2990-3135.

Cabeza,L.F., M.M.Taylor, G.L. Dimaio, E.M.Brown, W.N .Marmer, R. Carrio, P.J. Celma and J. Cot (1998c). Processing of leatherwaste: pilot scale studies on chrome shavings.Isolation of potentially valuable protein products and chromium., *Waste Management* 18: 211-218.

Cabeza, L.F., M.M. Taylor, E.M Brown, W.N. Marmer,R. Carrio, E. Grau, P.J Celma , J.Cot and AM Manich (1999). Treatment of sheepskin chrome shavings. Isolation of High Value protein products and reuse of chromium in the Tanning Process, *Journal of American Leather Chemists Association.,* 94: 268 -287.

Cot,J., A. Marsal, A. Manich, P. Celma, L.F. Cabeza, L. Labastida, J. Barenys, L. López and J.Salmerón(2003). Minimization of industrial wastes: adding value to collagenic materials. Procter memorial lecture. *Journal of Society of Leather Technologists and Chemists.*, 87: 91-97.

Crispim, A. and M.Mota (2003). Leather shaving treatment- an enzymatic approach**.** *Journal of the Society of Leather Technologists and Chemists.,* 87: 203-207.

Guardini, G. (1990). Extraction of Proteins and Chromium Sulphate from Chromium tanned Skins Wastes *US Patent* 4,483,82.

Gutterres M. and I.V Da Silva I (2010). Leather retanning with hydrolyzed protein. *Journal of American Leather Chemists Association,* 105: 195-197.

Heidmann E., (1991), Disposal and recycling of chome-tanned materials *Journal of American Leather Chemists Association.,* 86: 331-333.

Holloway D.F (1978). Recovery and Separation of Nutritious Protein Hydrolysate and Chromium from Chromed Leather Scrap *US Patent* 4,100,154.

Jianzhong, M., L. Lingyun, X.Chunhua, W. Wenqi and Y.Zongsui (2004). Protein retaining and filling agent from vinyl monomer graft modification of chrome shavings hydrolysate. *Journal of the Society of Leather Technologists and Chemists.,* 88: 1-5.

Kapusnaik, J., W. Ciesielski, J.J. Koziol and P.Tomasik (1999). Reaction of starch with □-amino acids.*Journal of European Food and Technology.,* 209: 325-329.

Langmaier, F, R.Mokrejs , R. Karnas, M. Mdalek and K.Kolomaznik (2006). Modification of chrome-tanned leather waste with epichlodhydrin. *Journal of the Society of Leather Technologists and Chemists* , 90: 29-34.

Manzo G. and G. Fedele (1994). Tanning action of condensates produced by chromed residues. *Das Leder.,* 45: 142-149.

Manzo G. and G. Fedele(1996). Separation by ultrafiltration of the different fractions of the collagenic condensate and study of their tanning properties. *Das Leder* ., 7: 66-73.

Morimura,S, H. Nagata, Y. Uemura, A. Fehmi, T. Shigematsu and K.Kida (2002). Development of an effective process for utilization of collagen from live stock and fish waste process *Biochemistry* 1403- 1412.

Mu,C. , W. Lin, M. Zhang and Q. Zhu(2003). Towards zero discharge of chromium-containing leather waste through improved alkali hydrolysis. *Waste Management.,* 23: 835-843.

Reis , A.D.M. and V Beleza(1991). Utilization of leather waste-animal feed stuff from chrome shavings: Part 1, Pilot Plant study. J*ournal of the Society of Leather Technologists and Chemists.*, 75: 15-19.

Santos, L.M., and M. Gutteres(2007). Reusing of hide waste for leather fatliquoring. *Journal of Cleaner production.,* 15:12-16.

Shenghua, L., O.R. Huijun , W. Jieliang and Y. Quanrong(2005). Synthesis and application of graft copolymer retannage of degraded starch and vinyl monomers. *Journal of Society of leather technolgists and Chemists*., 89: 63-66.

Shapcott, D. and J. Hubert (1979). "Chromium in Nutrition and Metabolism". Symposium on Chromium in Nutrition and *metabolism* 2, Eds., *Elsevier*, Amsterdam.

Spier, A. (2005). Fillers: valueable components in the retanning of leathers . *World leather*, 18: 28-35.

Sun,D., X. Liao, and B. Shi(2003). Oxidative dechroming of leather shavings under Ultrasound *Journal of the Society of Leather Technologists and Chemists.*, 87: 103 -106.

Tahiri,S, M. Bouhria, A.Albizane, M.A. Azzi, M.Alamiyounss, and J. Mabrour (2004) Extraction of proteins from chrome shavings with sodium hydroxide and reuse of chromium in the tanning process. *Journal of American Leather Chemists Association.,* 99: 16-25.

Taylor M.M , L.F. Cabeza , G.L. Dimaio, E.M. Brown , W.N. Marmer, R.Carrio, P.J. Celma and J.Cot (1998). Processing of leather waste: Pilot scale studies on chrome shavings: Part II Purification of chrome cake and tanning trials. *Journal of American Leather Chemists Association.,* 93: 83-98.

Taylor,M.M., W.N. Marmer and E.M . Brown (2004). Molecular weight distribution and functional properties of enzymatically modified commercial and experimental gelatins. *Journal of American Leather Chemists Association* 99: 133-144.

Zar, J.H., (1999). Biostatistical analysis .4th edition .Prentice Hall, Englewood Cliffs, New Jersey.

(*Accepted for publication November 2012*)