Hydrolysis of Chromium Tanned Leather Waste: Turning Waste into Valuable Materials – A Review

by

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Abstract

Among the reuse and/or disposal possibilities for chromium tanned leather waste (CTLW), one in particular stands out: hydrolysis. This process not only allows chromium recovery, but also the extraction of its protein, as collagen hydrolysate or as gelatin. CTLW hydrolysis has been performed for decades. However, industrial application of this important alternative has not been widespread. Thus, this review presents how CTLW alkaline hydrolysis has been evolving over the years; how the process can be adjusted to increase protein extraction yield and to produce better quality products. Finally, it reviews in which areas its products have already been tested. Here, researchers may find practical process information that might allow them to focus on the most important current issue for CTLW hydrolysis: how to upgrade this process to an industrial scale.

Introduction

The tanning industry is one of the first to use and recycle a secondary raw material: animal hides from slaughterhouses.[1-4] However, only about 20-25% (65% in sole leather production) of the raw salted bovine hide is transformed into leather, which makes the tanning industry also a considerable waste generator.[5]

From 80% to 90% of all tanneries use chromium Cr (III) salts in their processes.[5] Attempts have been made to replace it with other metals or with vegetable tanning. However, these alternatives were not able to provide physical properties (flexibility, tooling, burnishing character, and hydrothermal stability) as good as the ones provided by Cr (III) salts.[5-8] It is, therefore, unlikely that Cr (III) will be totally replaced in the near future.

Most chromium tanned leather wastes (CTLW) are produced in operations of trimming, splitting, shaving, and buffing, all of them post-tanning processes.[3, 4] About 75% of the CTLW is produced when tanned hide is shaved to a uniform thickness. One ton of raw hide typically generates 70-350 kg of fleshings (untanned), 225 kg of shavings, 150 kg of trimmings, and 2 kg of buffering dust (the three latter ones tanned). Also, for each ton of hides processed, 2-5 kg of chromium go to the liquid effluent.[9]

Even though conventional incineration or landfilling are simple disposal methods for CTLW, they may not be appropriate due to possible oxidation of Cr (III) to Cr (VI).[1, 6, 7, 10, 11] Also, direct use of CTLW as fertilizer and in the composite boards industry no longer seems to be the most suitable alternative due to high cost and/or environmental issues.[12] Therefore, other alternatives that deal with wastes generated in this industry should be explored.[10, 13-15]

Hydrolysis is an alternative method for CTLW use since it allows the extraction of two main fractions from it: protein and chromium. CTLW hydrolysis dates back to the 70's [16] and its broader development started in the 90's.[2, 17, 18] However, industrial application of CTLW hydrolysis depends on feasible uses for the resultant fractions.[11]

According to some authors, finding suitable applications for gelatin is easy if compared to the task of finding value-added uses for collagen hydrolysate.[19] Production cost for protein hydrolysates is not negligible, and it seems that applying this process in the industry is more an economic issue than a technical one.[20]

Taking the given information into consideration, the focus of this review will be the alkaline hydrolysis of CTLW, which allows for gelatin extraction. In order to assist future researchers to produce relevant new knowledge and focus mainly on product application, this paper brings information about how CTLW hydrolysis has been performed, and how its parameters can be adjusted for better extraction yield and/or product quality. It also lists applications for protein and chromium fractions extracted from CTLW, both suggested and already tested.

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CTLW Characterization

The composition of CTLW hydrolysis products depends directly on the composition of the waste used, which varies according to the quality/type of hide and according to the tanning process used, as it is shown in Table I.

Lower pH values for CTLW, for example, may indicate the need for higher alkalinizing agent quantity in order to reach pH high enough to hydrolyze the sample. Higher chromium amounts may result in a more stable CTLW, leading to the necessity of more aggressive hydrolysis conditions for protein extraction.

Therefore, hydrolysis parameters may have to be adjusted when different CTLW are used.[6, 23] Processing CTLW from different sources should result in lack of reproducibility. Direct comparisons between processes should also be done carefully, since apparently better or worse results may be only due to different CTLW composition.

CTLW Hydrolysis

There are three types of CTLW hydrolysis: acid, alkaline, and enzymatic, as presented in Figure 1.

Table I
Characterization of CTLW used for protein/chromium extraction through hydrolysis.

pH	Cr_2O_3 (%)[a]	Moisture (%)	Ash (%)[a]	TKN (%)[a]	Fat (%)[a]	Reference
4.39	--	6-10	13	18.4	2.1	21
3.5	4.7	54.1	9.9	15.0	--	22
3.8	4.21	53.51	14.32	14.54	0.09	23 A[b]
4.2	4.28	53.47	8.40	14.56	1.51	23 B[c]
3.6	3.99	51.47	14.95	14.13	1.79	23 C
3.45	3.27	53.12	10.33	16.45	0.65	2 A[d]
3.87	3.01	50.52	10.52	16.59	0.86	2 B[d]
3.34	2.74	53.58	7.38	14.47	--	24
--	4.5	31.0	11.0	20.0		20
3.55	2.39	51.5	8.5	13.0	--	25

[a]On a dry matter basis
[b]Samples from a conventional chrome tannery
[c]Sample from a process which uses high exhaust chrome treatment
[d]Samples obtained from the same tannery, but from different drums, later mixed for hydrolysis process.

Acid hydrolysis results in a chromium-rich liquid and in a solid cake with low chromium content. Hydrochloric, sulfuric, citric or acetic acid may be used for periods that vary from 2 h to 6 days and temperatures from 23 to 70°C.[26-28] Up to 60% of chromium was recovered through acid hydrolysis of CTLW by Ferreira *et al.*[26] This chromium-rich hydrolysate may be used in retanning or leather finishing.[29]

Alkaline hydrolysis of CTLW usually produces gelatin or hydrolyzed collagen in aqueous medium (with low chromium-content), and a solid chromium cake (rich in chromium).[12] Collagen hydrolysate is produced when more aggressive conditions (higher temperature, time or pH) are employed, which results in protein degradation. While collagen hydrolysate has molar mass in the range from 15 – 50 kg/mol, gelatin has a molar mass that ranges from 50 to 200 kg/mol.[1, 30, 31]

In its turn, enzymatic hydrolysis is performed in two steps: a chemical pre-treatment followed by the enzyme addition. In this case, gelatin is usually produced after the first step, while collagen hydrolysate is produced after enzyme addition. Production cost of enzymatic hydrolysis is higher than the one of alkaline hydrolysis since an additional step is added and, besides enzyme addition, higher amounts of chemicals have to be added as well. However, protein extraction yield is increased.[1, 3, 31-33]

Protein extraction from collagenic materials (such as animal hides, skins, or bones) involves the breakage of cross-links responsible for collagen stabilization and insolubility.[34] However, when the collagen structure of animal hides/skins is tanned with chromium salts to produce leather, not only native collagen cross-links, but also the chemical bonds of the collagen-chromium complex (shown in Figure 2), have to be broken. The collagen-chromium complex, as stated by Mancopes *et al.*,[35] is formed through a chemical reaction between chromium (III) complexes and the carboxyl groups of aspartic and glutamic acids (amino acids of collagen structure). Both collagen-chromium complex and collagen cross-link bonds can be broken through hydrolysis.

CTLW Alkaline Hydrolysis

Alkaline hydrolysis of CTLW results in a protein fraction in aqueous medium (usually with low chromium content, since this metal precipitates as $Cr(OH)_3$ in high pH values) and in a chrome cake. In this paper, focus will be given for processes that aimed at protein extraction. It must be highlighted, however, that alkaline hydrolysis may be used to solubilize collagen and chromium, with no worries about keeping protein structure.[36, 37]

Some of the factors that directly affect alkaline hydrolysis are the type and mass of alkalinizing agent, pH, temperature, and process time. Table II shows some conditions used in CTLW alkaline hydrolysis and Table III shows the characterization of its product of interest: the protein fraction (gelatin or collagen hydrolysate).

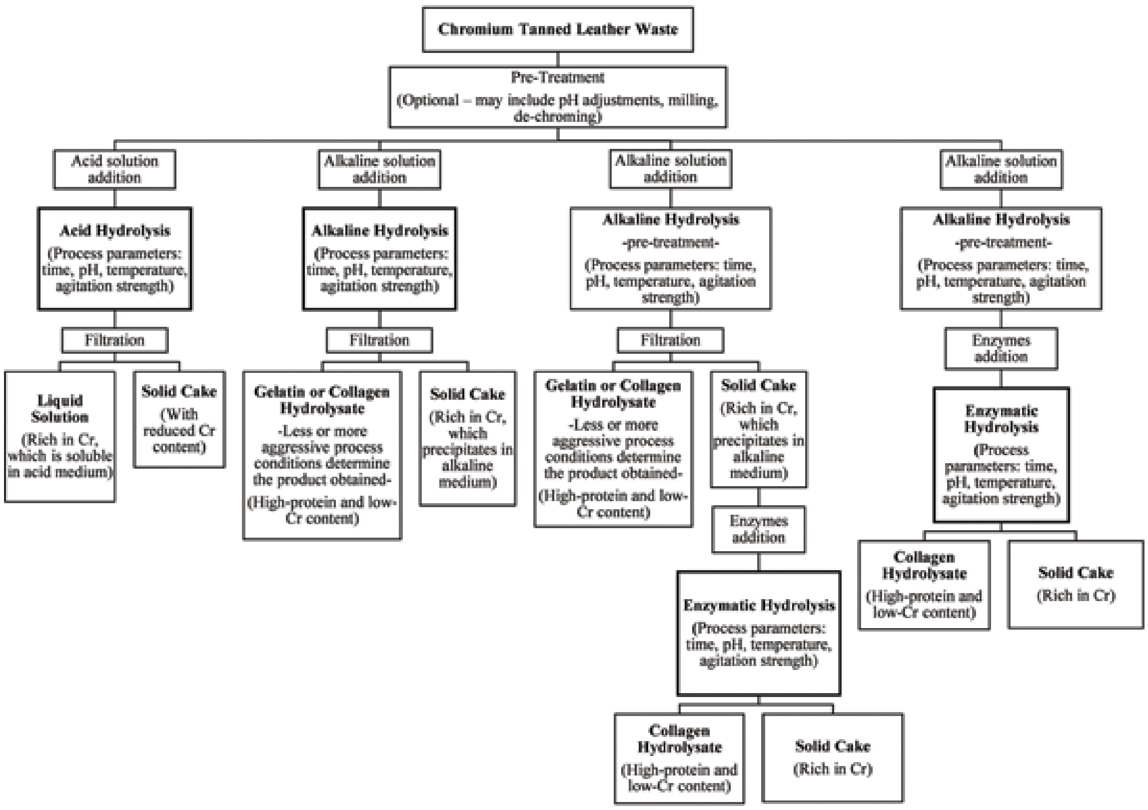

Figure 1. CTLW hydrolysis different processes and their production

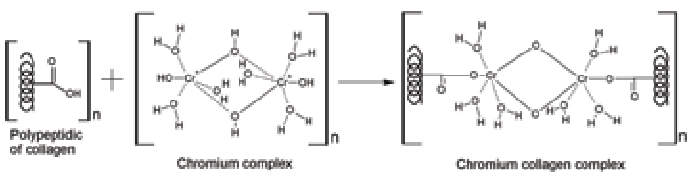

Figure 2 - Chromium-collagen reaction during tanning process.

Extraction Yield and Protein Quality

As it is seen in Table III, protein extraction yield was not higher than 75% in any of the presented studies. Mu *et al.*[3] indicate some possible reasons for the incomplete hydrolysis of CTLW under alkaline conditions. The first is the presence of non-polar and alkaline amino acids, that are hydrophobic under alkaline conditions and therefore do not allow water to penetrate into their structure and thus are not hydrolyzed. The presence of covalent bridges between alkaline amino acids and hydroxyl amino acids, which are only broken in acid conditions, may also explain non-complete hydrolysis. Finally, still according to the same authors, chromium (III) complexes that are formed under alkaline conditions (during basification) may crosslink with carboxyl groups, resulting in insoluble macromolecular metal complexes.

High molar mass of protein extracted by Cabeza *et al.*[30] and Taylor *et al.*[32] (69% > 50 kg/mol) indicate that gelatin is extracted when process conditions tested by the authors are employed. On its turn, Ting-Da *et al.*[33] obtained collagen hydrolysate from CTLW and showed that, when used the same pH and temperature values, protein with lower molar mass is extracted when process time is increased. The reduction in molar mass is followed by an increase in protein extraction yield.

Mu *et al.*[3] showed that a second extraction from the chrome cake obtained after the first CTLW hydrolysis results in a protein with lower molar mass. It reduces from 40 – 110 kg/mol to 10 – 50 kg/mol. The first extraction, therefore, results in gelatin in aqueous medium, while the second extraction results in collagen hydrolysate.

Alkalinizing Agent and pH

Among the alkalinizing agents used for CTLW hydrolysis, CaO seems to have the advantage of being less expensive. The lime milk produced by it also seems to adsorb the small $Cr(OH)_3$ particles, facilitating their removal through filtration.[3,33] Diluted suspensions of CaO precipitate simultaneously most of sulphate ions as calcium sulphate together with chromium hydroxide. This co-precipitation also increases the separation yield and the rate of finely precipitated chromium hydroxide.[38] CaO is also a stronger alkalinizing agent, which results in higher pH values achieved with lower amounts of it, which means cost reduction.[25,33] Finally, if protein obtained from CTLW hydrolysis is used for animal feeding purposes, the calcium demand is higher than the sodium or magnesium ones.[33] In its turn, NaOH as alkalinizing agent may lead to a fast pH increase and consequent digestion of collagen, reducing its molar mass.[3]

Table II
Tested parameters for CTLW alkaline hydrolysis

Test code	CTLW mass (g)	Water/solution volume (mL)	Alkalinizing Agent	pH	Temperature (°C)	Time (h)	Reference
A	1000	5000	MgO – 6%	8 a 9	72	6	30, 32
B	-	-	CaO	7,8 / 10,1 / 11,0 / 11,3 / 11,8	90	10	33
C	-	-	-	-	65 / 75 / 85 / 95	-	33
D	-	-	-	-	-	2 / 4 / 8 / 12	33
E	100	1000	CaO – 10 g	-	98	3 / 6 / 24	3
F	100	1000	MgO – 10 g	-	98	3 / 6 / 24	3
G	100	1000	NaOH – 10 g	-	98	3 / 6 / 24	3
H	100	1000	CaO/NaOH	11	79-80	3,5	3
I	Resultant cake from process "H"	100	CaO – 2 g	--	97-99	3 a 4	3
J (repeating the process 4 x, using previous process cake)	100	1000	CaO – 10 g	-	98	3	3
K	50	250	NaOH / MgO	9	70	15	31
L	50	250	CaO – 2 g	-	70	6	25
M	50	250	MgO – 2 g	-	70	6	25
N	50	250	CaO – 4 g	-	70	6	25
O	50	250	MgO – 4 g	-	70	6	25

In order to have a process in which low amounts of chromium is solubilized in the protein fraction, pH values for CTLW alkaline hydrolysis should be lower than 11.[33] Niculescu *et al.*[38] indicated that the appropriate ratio for alkaline agent/hydrolyzing material should be equal to two parts of CaO to one part of chromium in leather wastes. According the authors, in this condition, the whole amounts of chromium from the hydrolyzing material precipitates with the chrome cake.

Time and Temperature

Higher temperatures increase protein extraction rate, but also accelerate protein decomposition rate and increase the amount of chromium dissolved (which increases exponentially with temperature).[25, 33, 39]

According to Ting-Da *et al.*[33] CTLW alkaline hydrolysis occurs in two steps: OH^- goes inside after impregnation and swelling of CTLW, and then it breaks the cross-links between collagen and Cr (III). Therefore, long periods of hydrolysis, longer than the necessary time for both steps described, are not responsible for protein extraction, causing only protein hydrolysis, reducing its molar weight and increasing chromium dissolution. This is corroborated by Niculescu *et al.*,[38] who shows that at temperature values higher than 80°C, hydrolysis processes of more than three hours result in similar protein extraction yield and lower molar weight of the product. However, when it comes to chromium dissolution, in a work by Wionczyk *et al.*,[39] it is shown that after 6 h of hydrolysis (with 0.2 M and 0.3 solution of NaOH, at 60 and 70°C), the amount of chromium in the solution is reduced. It is said to happen due to the hydrolysis of soluble hydroxocomplexes of chromium (III) to insoluble chromium (III), leading to a different conclusion from the one obtained by Ting-Da *et al.*[33]

Table III

Characterization of protein from CTLW alkaline hydrolysis performed as described in Table II.

Test code	Chromium (mg/L)	Total Kjeldah Nitrogen (g/L)	pH	Ashes (% dry basis)	Dry mass (%)	Molar mass (kg/mol)	Protein extraction yield (%)	Reference
A	12,5	17,35	9,1	17,33	3,54	47% > 85 22% >50 and < 85 31% < 50	30	30, 32
B	0,25 (pH 7,8) 3,4 (pH 10,1) 3,5 (pH 11,0) 16,5 (pH 11,3) 23,3 (pH 11,8)	11,0 (pH 7,8) 13,5 (pH 10,1) 15,0 (pH 11,0) 29,9 (pH 11,3) 32,4 (pH 11,8)	-	-	-	-	-	33
C	≈ 0,2 (65°C) ≈ 0,7 (75°C) ≈ 2 (85°C) ≈ 7 (95°C)	≈ 5,7 (65°C) ≈ 6,5 (75°C) ≈ 9,0 (85°C) ≈ 15 (95°C)	-	-	-	-	-	33
D	< 0,1 (2 h) ≈ 0,1 (4 h) ≈ 0,6 (8 h) ≈ 10 (12 h)	≈ 13 (2 h) ≈ 17 (4 h) ≈ 21 (8 h) ≈ 27 (12 h)	-	-	-	16,6 (2 h) 13,9 (4 h) 9,2 (8 h) 8,4 (12 h)		33
E	-	-	-	-	-	-	46,5 (3h) 68,0 (6h) 69,5 (24h)	3
F	-	-	-	-	-	-	38,6 (3h) 59,8 (6h) 65,4 (24h)	3
G	-	-	-	-	-	-	48,2 (3h) 69,8 (6h) 71,9 (24h)	3
H	-	17,4	6	6,3	-	40 – 110	-	3
I	-	16,9	6	8,2	-	10 – 50	-	3
J	-	-	-	-	-	-	75[a]	3
K	0,396 (NaOH) 0,133% (MgO)	n.d. (NaOH) 0,35% (MgO)	-	-	-	-	-	31
L	38,7	9,4	11,6	12,2	6,7	-	48,7	25
M	< 0,04	2,2	9,2	21,6	2,4	-	9,2	25
N	0,44	10,8	13,8	11,7	7,9	Sample did not turn into gel at 4°C – degraded sample	74,5	25
O	< 0,04	2,1	9,9	25,5	2,3	-	8,3	25

[a] After second extraction, no increase in yield reported after it

Table IV
Suggested and tested applications for products obtained from alkaline hydrolysis of CTLW.

Application	Suggested/Tested	Reference
Gelatin		
Cosmetics, printing, adhesive, photography, microencapsulation, films, additives in finishing products for the leather industry	Suggested	30
Microencapsulation	Tested	40
Animal feed	Suggested	33
Cosmetics, printing, adhesive, photography	Suggested	21
Cosmetics, printing, adhesive, photography, microencapsulation, films	Suggested	6
Gels, adhesives, photographic substrates, printing	Suggested	20
Finishing agent of glazed leather	Tested	10
Films	Tested[1]	41
Poultry feed	Tested	42
Films	Tested	25
Hydrolyzed collagen		
Organic nitrogenous fertilizer, biodegradable polymers for agriculture uses (sowing tapes), adhesives, anti-skid agents in PVC and rubber compounds, additive to concrete	Tested	43
Leather retanning agent	Tested	15
Films	Suggested	44
Pretanage added to pickle float	Tested	14
Feed additive, nitrogenous fertilizer, raw material for preparing adhesives, corrosion inhibitors	Suggested	20
Hydrogels	Tested	45
Films	Tested	46
Leather retanning	Tested	47
Foliar biofertilizers with protein additives for plant growth	Tested	22
Microencapsulation	Tested	48, 49
Base for polyacrylamide flocculants	Tested	50
Adhesives	Tested	51
Poultry feed	Tested	52
Chromium salts (extracted from chrome cake)		
Pigments for glassmaking, manufacture of heat resistant bricks, production of alkaline chromate	Suggested[2]	43
Tanning agent	Tested	18
Tanning agent	Suggested	33

[1]Only the cross-linking process tested • [2]production of alkaline chromate tested

Application of the Fractions Obtained from CTLW Hydrolysis

Some applications for gelatin, collagen hydrolysate, and chromium recovered from chrome cake have been suggested and, some of them, tested, as shown in Table IV.

Due to the presence of chromium and the origin of the product (a waste), protein extracted from CTLW cannot be used in the food industry. However, for technical purposes, gelatin and collagen hydrolysate from CTWL hydrolysis are still promising, as well as the chromium salts recovered from it.

Conclusion

This review has addressed how CTLW alkaline hydrolysis is used for protein extraction and how the process parameters may be changed in order to achieve better process yield and/or product quality. In addition, possible uses for protein and chromium extracted from CTLW are listed. The authors think; therefore, they have provided extensive material to help future researchers test and create new feasible application for these products, without needing to focus their studies on extraction process conditions.

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