ADVANCED AND CLEAN TECHNOLOGIES FOR CHROMIUM TANNED LEATHER WASTE RECYCLING AND GREEN ENERGY PRODUCTION

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Abstract: *Chromium tanned leather wastes are difficult to valorise by chemical and biological processes due to the strong bonds established between collagen and chromium. Thus a one-step fast clean pressure-assisted alkaline hydrolysis method has been studied to disrupt recalcitrant bonds. The effects of calcium oxide, temperature, time, liquid to solid ratio and leather scrap size on organic matrix destruction, chromium dissolution and anaerobic biodegradability of hydrolyzates obtained were evaluated. The results show that pressure-assisted hydrolysis with CaO may be a good alternative to reduce leather waste volume, obtain biodegradable solutions with low Cr concentration and final residues usable as a chromium bearing resource. In the optimised conditions, about 50% to 55% of the leather is dissolved. The slurries obtained contain above 90% of the chromium. The hydrolyzates show good anaerobic biodegradability mostly in the range of 50% to 70 %, indicating them as a source of biogas.*

Keywords: *Waste, leather, chromium, alkaline de-chroming, anaerobic biodegradation.*

1. INTRODUCTION

The treatment of chromium-containing leather waste, mainly bovine shavings, by alkaline hydrolysis with calcium salts has been studied to obtain protein hydrolyzates with low chromium content and a chromium rich cake [1–3]. A lab scale study proposing a three-step process to treat pigskin chromium tanned leather waste and separate the protein and chromium fractions has also been reported [4]. Various alkali and enzymatic hydrolysis were compared and calcium oxide alone was found to be more effective for the purposes pursued over magnesium oxide, sodium hydroxide and enzymes plus magnesium oxide [4]. A study on leather wastes hydrolysis with CaO (temperatures ranging from 343 K to 371 K for up to six hours in one or two steps) and other study on alkaline CaO hydrolysis followed by enzymatic hydrolysis (temperatures ranging 310 K to 343 K up to four hours of holding time) have been reported, to obtain an hydrolyzate with average molecular mass below 10 kDa and low chromium content [5]. Some of these processes have been scaled-up [6–11].

Alkaline hydrolysis above atmospheric pressure has also been the object of some studies. Temperatures reported range 373 K to 573 K, pressures are till 15 MPa, and the alkaline agents used include calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide or sodium hydroxide [12–17].
Alkaline hydrolysis plants at industrial scale are in small number, however an excess of hydrolyzate production is reported [18, 19]. Therefore, research on more applications is needed and one is exploring hydrolyzate biodegradability through anaerobic digestion, thus contributing to use its potential for producing biogas.

The biodegradability of tanning chemicals, natural tannin extracts [20–24], fatliquors [25, 26], surfactants [27], tanning agents [28, 29] and finishing resins [27], has been studied. Biomethanization of tannery waste, especially wastewater treatment sludge and wastes from pretanning processes steps has also been the object of several successful reports [30–45]. The biodegradability of chromium tanned leather and vegetable tanned leather under anaerobic conditions has been addressed, too [46, 47]. In the studied conditions, it has been found that vegetable tanned leather leads to more gas production than chromium tanned leather and detanning tends to improve biodegradability of both types of leathers [46]. The study of biopolymers as tanning agents to develop biodegradable leathers is a global trend in leather industries [48–50]. The

anaerobic biodegradability of protein hydrolyzates resulting from alkaline enzymatic hydrolysis has also been studied in the following conditions: i) modifying polyvinyl alcohol which had been processed into water-soluble films often employed in agriculture [51, 52]; ii) cross-linked with dialdehydes [53] ; iii) cross-linked with higher-molecular weight diepoxides, which have the potential to be biodegradable films [54]. The effect of anaerobic digestion at 323 K for 15 days on deproteination of chromium sludge resulting from a two-step alkaline enzymatic hydrolysis has also been reported [55]. In many of these works biodegradability reported is based in BOD/COD ratio.

The present work evaluates the application of one short time wet alkaline treatment at relatively mild temperature and pressure to the finished leather scrap from footwear manufacturing; it aims at recovering chromium with maximum organic matrix attack and minimum chromium dissolution, followed by organic biodegradation of the liquid phase obtained. The effect of temperature, time, CaO concentration and leather size on both chromium and organic matter recoveries was studied. Anaerobic biodegradability of the resulting liquid phases was assessed based on established standards and quantification approaches.

2. EXPERIMENTAL

2.1 Materials and reagents

Seven bovine finished chromium-tanned leathers presenting general properties usual in shoe manufacture were collected. Calcium oxide and other reagents used were of adequate analytical grade.

2.2 Sample preparation

For the pressure-assisted hydrolysis tests the leather samples were shredded to ≤ 1 and 2 mm using a Pegasil® – Zipor® mill with rotating knives or cut by hand to 1 cm x 1 cm pieces, thoroughly homogenized and conditioned in standard laboratory atmosphere at 296 K ± 2 K and 50 % ± 5% relative humidity. For chemical characterization the material was shredded to ≤ 4 mm.

2.3 Pressure-assisted alkaline hydrolysis tests

The pressure-assisted hydrolysis tests were done at least in triplicate using a titanium laboratory autoclave model 4842 from Parr® (Moline, Illinois, USA) with a 400 mL reaction vessel and no stirring action. The liquids were immediately characterized or frozen at 253 K ± 2 K and the residues were dried at 373 K ± 2 K and calcinated at 1173 K ± 5 K for characterization. The experimental plan followed is presented in Table 1.

Table 1: Experimental plan

Set series	Test	Tempe-rature, K	Leather size, mm	Liquid to solid ratio, mL:g	Holding time, min.	CaO, g
First	T1.1; T1.2; T1.3	373	≤ 2	6.67	45; 90; 180	0.75
	T1.4; T1.5; T1.6; T1.7			10	15; 45; 90; 180	0.38
Second	T2.1; T2.2; T2.3	403	≤ 2	6.67	45; 90; 180	0.75
	T2.4; T2.5; T2.6; T2.7; T2.7; T2.9				90	0.38; 0.75; 1.13; 1.50; 1.88; 2.26
Third	T3.1; T3.2; T3.3	423	≤ 2	6.67	45; 90; 180	0.75
	T3.4; T3.5; T3.6; T3.7; T3.8; T3.9		≤ 2		90	0.38; 0.75; 1.13; 1.50; 1.88; 2.26
	T3.10; T3.11; T3.12		≤ 1; ≤ 2 10 x 10		90	0.75
Fourth	T4.1; T4.2; T4.3	443	≤ 2	6.67	45; 90; 180	0.75
	T4.4; T4.5; T4.6; T4.7; T4.8; T4.9				90	0.38; 0.75; 1.13; 1.50; 1.88; 2.26

2.4 Anaerobic biodegradation tests of hydrolyzates

Liquid phases from selected leather hydrolysis tests, as well as gelatine and standard cellulose material Avicel® from Fluka® were subjected to anaerobic biodegradation tests using sludge from leather factory "Curtumes Aveneda" anaerobic wastewater treatment plant and following an internal method based in ISO 11734:1995 [56]. Measurement of biogas and calculations were done using the WTW OxiTop® Control measuring system according to Süßmuth et al., 1999 [57].
In this method, the total coefficient of degradation is calculated according to:

$$D_t = [(n_{CO2,g;CH4,g} + n_{CO2,l})/n_{C,theo}] \times 100\% \quad (1)$$

Where: D_t – coefficient of total biological degradation, in percentage; $n_{CO2,g;CH4,g}$ – number of moles of carbon dioxide and methane gases formed; $n_{CO2,l}$ – number of moles of carbon from carbon dioxide formed in the aqueous phase; and $n_{C,theo}$ – theoretical number of moles of carbon in the test solution or material.

2.5 Analytical procedures

The chromium tanned leather sample shredded to ≤ 4 mm, the alkaline hydrolysis liquids obtained and the dried residues were chemically characterized following standards listed in Table 2 [58–66].

Table 2: Chemical methods to characterize leather samples, hydrolysis solutions and residues [58–66]

Parameter	Method
pH	ISO 4045:2008
Volatile matter	ISO 4684:2005
Total ash at 1173 K	-
Total organic carbon	EN 13137:2001
Total Cr	Digestion US EPA 3050B:1996 and Atomic Absorption Spectroscopy
Calcium	Standard Methods for Examination of Waters and Waste-Water 2003
Hexavalent chromium	ISO 17075:2007
Azo colorants	ISO 17234-1:2010
Pentachlorophenol	ISO 17070:2006

3. RESULTS AND DISCUSSION

3.1 Sample chemical characteristics

The leather material used in the hydrolysis tests has pH of 3.5 ± 0.1, (4.0 ± 0.1) % of ash, (53.1 ± 0.5) % of total organic carbon (TOC), 2.0 % of Cr and 0.6 % of Ca. Hexavalent chromium, amines and pentachlorophenol are below threshold value (<3 mg/kg, <30 mg/kg and <5 mg/kg, respectively).

3.2 Alkaline hydrolysis tests results

Fig. 1 summarizes the results obtained in the first set of experiments (T1.1 to T1.7). Leather hydrolysis at 373 K for 15 to 180 minutes with liquid to solid ratio of 6.67 or 10, gave higher TOC recoveries for longer holding times and higher liquid to solid ratio. The hydrolyzates are brown liquids containing 7 g/L to 27 g/L of TOC and 5 mg/L to 20 mg/L of Cr. Approximately 10 % to 20 % of the initial TOC and below 1 % of chromium, respectively, were recovered in that liquid phase.

In these test conditions, resulted residues having 73 % to 93 % of the original leather weight which contain total chromium below 3 %. The ashes obtained after calcination of those residues at 1173 K for 2 hours present chromium expressed as Cr_2O_3 and calcium expressed as CaO in the range of 14 % to 24 % and 24 % to 29 %, respectively.

Globally, this first set of tests indicates poor mass waste reduction under these conditions. Other authors [1-5], as well as tests done in our laboratory, indicated much faster leather destruction using NaOH even though with higher chromium concentration in the solutions and more difficulties to filtrate them [67].

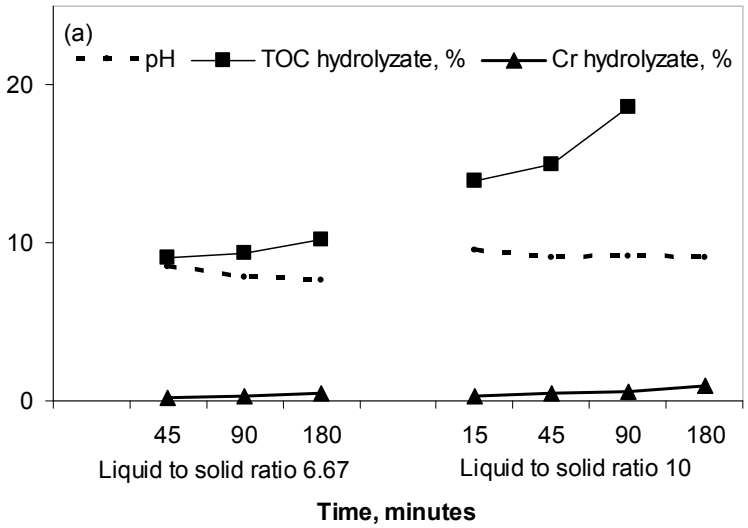

Figure 1: Results obtained in the first experimental tests T1.1 to T1.7

Fig. 2 shows the effects of temperature and holding time (T2.1 to T2.3, T3.1 to T3.3 and T4.1 to T4.3 tests) in the hydrolysis characteristics. Hydrolysis at 403 K promotes chromium dissolution that reaches 1 % to 3 % of the Cr available in the leather sample. TOC recovered reaches 30 % to 43 % of the available TOC, depending on the hydrolysis conditions. At 423 K leather matrix destruction is higher than at 403 K and reaches 50 % of the initial leather mass with only 4 % Cr dissolution. At 443 K, TOC concentration in the hydrolyzate ranges 50 % to 55 % and Cr concentration in it is always above 6 % reaching 11 % for the longer holding time.

In these tests, the mass of the residue obtained is in general 40 % to 60 % of the leather mass treated. The solid residues from most of the tests gave ashes with around 30 % Cr as Cr_2O_3 and 22 % to 25 % of CaO, thus are interesting as a source of Cr for some industrial applications, since they are in the normal range of common chromite concentrates.

The results of all these hydrolysis tests show that hydrolysis solutions final pH may be explained by effective CaO addition (CaO, g) and liquid to solid ratio (L/S, mL:g)) through the equation pH = 3.20 + 0.74 CaO + 0.45 L/S. The quality indicators of this regression are R^2 = 0.81, F = 53.19 with p < 0.00000, thus indicating that the equation that relates the variables has not only statistical significance but also high physical/experimental significance.

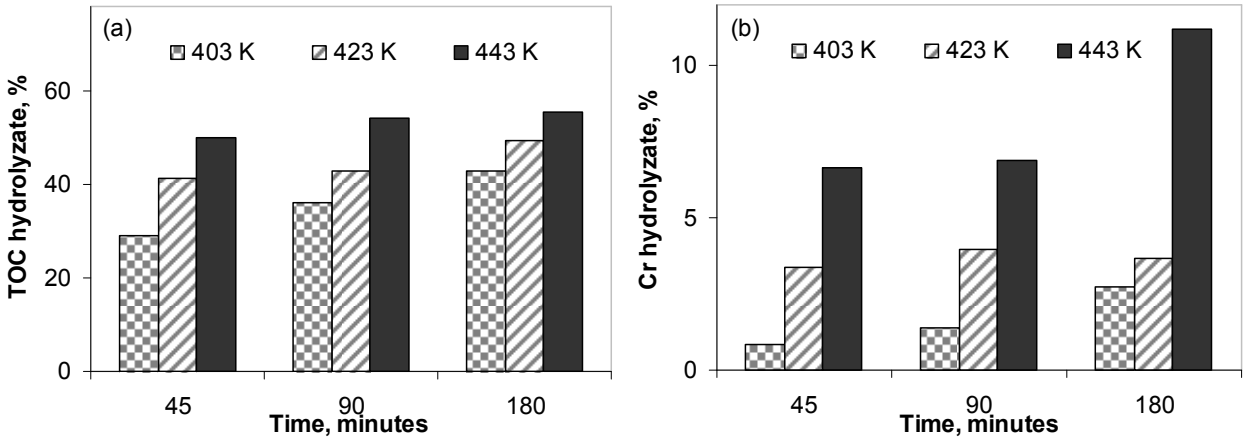

Figure 2: Comparing the effect of temperature and holding time for tests T2.3 to T2.5 at 403 K, T3.1 to T3.3 at 423 K and T4.1 to T4.3 at 443 K, respectively for 45, 90 and 180 minutes

Fig. 3 presents the effect of temperature and CaO concentration in tests with 90 minutes of holding time (T2.4 to T2.9, T3.4 to T3.9 and T4.4 to T4.9 tests). These results indicate that by increasing temperature and CaO addition leather dissolution increases, particularly till 1.50 g CaO per 100 mL solution. Above this

concentration the effects are less pronounced. Fig. 3 (b) indicates temperature as having strong influence in chromium dissolution thus suggesting selection of lower temperature conditions for less chromium in solution. Adding above 1.13 g of CaO in the 423 K and 443 K hydrolysis tests had no relevant effect in residue reduction. Furthermore, addition of CaO above 0.75 g up to 1.13 g has a relative consumption decrease in the alkalis, therefore lowering Cr_2O_3 concentration in the ashes significantly below the 30 % target.

The most interesting results for the purpose of ensuring reasonable leather organic matrix destruction with relatively low chromium dissolution, generating calcinated residues having above 30 % Cr_2O_3, seems to be those obtainable under the following hydrolysis conditions: i) for 45 or 90 minutes at 423 K with 0.75 g CaO addition; ii) for 90 minutes at 423 K with 1.13 g CaO addition; iii) for 90 minutes at 443 K with 0.38 g CaO addition; and, iv) at 443 K with 0.75 g CaO addition and holding time of 45 minutes.

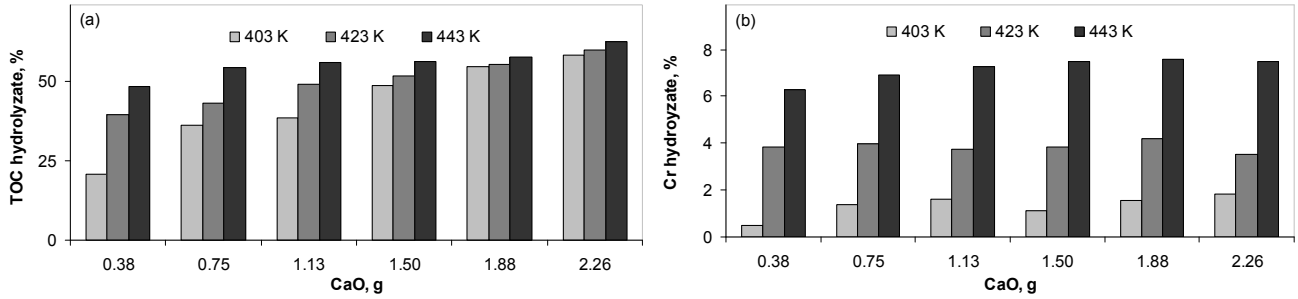

Figure 3: Comparing the effect of temperature and CaO concentration for 90 minutes holding time for tests T2.4 to T2.9 at 403 K, T3.4 to T3.9 at 423 K and T4.4 to T4.9 at 443 K, respectively for 0.38 g, 0.75 g, 1.13 g, 1.50 g, 1.88 g and 2.26 g of CaO addition

Leather wastes are generated in footwear industry as scraps presenting random shape and size. Due to its intrinsic fibrous nature leather grinding is a costly step that must be avoided if possible. Tests T3.10 to T3.12 evaluated the effect of leather size on leather dissolution at 423 K for 90 minutes with 0.75 g CaO addition. The preliminary results obtained indicate that 2 mm size may be a good compromise option for organic matrix destruction. However, this aspect needs to be explored in potential applications.

According the objectives established for this work globally the results obtained seem to indicate that the preferred options for hydrolysis treatment correspond to a ratio of 150 g of leather per 1000 mL water either at 423 K for 90 minutes with 11.3 g CaO addition (as T3.6) or at 443 K for 45 minutes with 7.5 g CaO (as T4.5). The solid residues obtained present lower volume than the original waste. Also, despite the relatively mild pressure and temperature used in these experiments, final solid residue has a mass of the same order of magnitude than the obtained by treatments at boiling temperature under longer times [1-5]. Fig. 4 presents images of initial grinded leather and the equivalent dehydrated sludge obtained for test T3.6.

Figure 4: Effect of CaO hydrolysis on leather volume for test T3.6: initial material and dehydrated sludge

The hydrolyzates and the solid residues obtained from the test T3.6 were characterized regarding Cr(VI), amines and pentachlorophenol. Amines and pentachlorophenol were neither detected in liquid samples nor in the solids. Cr(VI) in the solution was 0.4 mg/L ± 0.1 mg/L and in the solid 7.3 mg ± 0.4 mg of Cr(VI)/kg.

3.3 Biodegradability tests results

In the test conditions studied the coefficient of total anaerobic biological degradation, D_t, as defined by the expression (1), was above 70 % in 90 days for standard cellulose material and gelatine. Hydrolyzates from tests T3.3, T3.4 and T3.6 and T4.2, T4.3 and T4.5, obtained at 423 K or 453 K, gave D_t of 55 % to 65 %, 60 % to 70 %, 50 % to 60 % and 20 % to 30 %, 60 % to 70 %, 50 % to 60 %, respectively. Therefore, despite the variability of the results, the influence of the hydrolysis conditions on the anaerobic biodegradability of the resulting hydrolyzate is small. The D_t obtained ranged 20 % to 70 %.

4 CONCLUSIONS

Mild pressure-assisted alkaline hydrolysis with CaO may be an alternative to reduce the leather waste volume to manage, obtain biodegradable solutions with low Cr concentration and final residues usable as a chromium bearing resource.
Adequate conditions for this treatment are 150 g of leather in 1000 mL water heated for 45 minutes at: (i) 423 K with a 11.3 g CaO addition; or (ii) 443 K when 7.5 g CaO is added. In these conditions over 50 % of leather matrix and less than 6 % of total chromium were dissolved.
The hydrolysis temperature and conditions proposed are moderate and the alkaline hydrolysis reagent is common and relatively inexpensive. The hydrolysis process could be heated at the company level by using vapour as heating source or solar energy, since the temperature needed is relatively low.
The resulting hydrolyzates present good filterability and anaerobic biodegradability mostly in the range of 60 % ± 10 %, indicating them as a source of biogas as a feedstock of an anaerobic co-digestor preferably existing in the proximities.
The solid residues obtained after calcination may be attractive as a chromium resource.
Globally, CaO mild pressure-assisted hydrolysis contributes to reduce the leather waste volume to manage, obtain solutions with low Cr concentration that present reasonable anaerobic biodegradability and give value to the ultimate residue as a chromium bearing raw material.

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