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Alkaline Hydrolysis of Chromium Tanned Leather Scrap Fibers and Anaerobic Biodegradation of the Products

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Abstract

Chromium tanned leather wastes fibers are difficult to manage by chemical and biological processes due to the strong bonds established between collagen and chromium. Therefore, it is of great interest to develop treatments that disrupt recalcitrant bonds and may open new perspectives to materials valorization. A temperature and pressure-assisted alkaline hydrolysis method has been studied. The effects of sodium hydroxide concentration, temperature, holding time and leather fibers to solution ratio on organic matrix destruction, chromium dissolution and anaerobic biodegradability of hydrolyzates obtained are reported. The more suitable conditions found are leather fibers treatment at 423 K for 1.5 h with NaOH 4 mol/L solution and solid to liquid (S/L) ratio (w/w) of 0.15 or 0.2. Under these conditions, more than 98 % of the leather and 85 % of chromium were dissolved. The hydrolyzates may be used in the leather process and show anaerobic biodegradability mostly in the range of 20–30 %. This work establishes an alternative route of treatment that promotes fast destruction of chromium tanned leather scrap, and may avoid its landfilling, contributing to recover part of resources contained in leather waste.

Keywords Waste treatment · Leather · Chromium · Alkaline pressure hydrolysis · Anaerobic biodegradation

Introduction

In European footwear industry, over 70 % of the leather shoes produced use chromium-tanned leather for the upper part. Despite the many methodologies and systems studied and implemented in the last decades, which allowed the minimization of wastes during the leather and shoe production activities, production processes inevitably generate chromium tanned solid wastes. In the leather industry, only 20–35 % of the wet salted hide material is converted into useful leather, therefore in Europe, the annual cost of treating tannery waste was calculated as approximately 700 million € [1, 2]. In the European shoe industry, about 1×10^5–2×10^5 metric tones of leather waste are generated per year, thus, the annual cost supported by the sector for its management may reach 10 million € [3].

Chromium-tanned leather wastes have been the object of hundreds of studies, with the goal of recycling them. However, landfilling continues to be the preferred option for their management. This option wastes all the resources contained in the material. Thus, more sustainable alternatives for chromium-tanned leather scrap valorization are needed.

Various alkaline hydrolysis treatments have been studied for leather dechroming or dissolution [4–21]. These studies compared the influence on chromium recovery without or with leather matrix dissolution of some alkaline agents as sodium hydroxide, calcium hydroxide, sodium carbonate, magnesium oxide, potassium hydroxide, potassium tartrate, potassium carbonate and organic amines, alone or in combination, as well as different enzymes; at temperatures mostly in the range of 350 ± 20 K, and relatively long periods of treatment of 3–10 h up to 72 h. In general, these treatments involve several batches, frequently 2 or 3 but also up to 9 and manage to achieve chromium recoveries of up to 80 ± 15 %; however, the remaining materials still contain strongly bounded chromium to protein. Some of these processes have been scaled-up or industrialized [5, 7, 22].

Successive multiple alkaline treatments followed by acid treatments have also been proposed to separate the collagen and chromium fractions [23, 24]. The use of acids for further hydrolyzing alkaline hydrolyzates to prepare low-molecular weight products has also been reported [25]. Alkaline hydrolysis at higher temperatures and pressures has also been investigated. Leather shavings treatment at 573 K and 15 MPa in the presence of magnesium oxide for chromium recovery [26] has been proposed. The leather scraps may also be heated from 423 to 573 K at high pressure either in the presence or in absence of $Mg(OH)_2$ to recover Cr and collagen hydrolyzate [27, 28]. The preparation of protein hydrolyzate using calcium oxide and calcium hydroxide with or without magnesium oxide and magnesium hydroxide, sodium hydroxide, magnesium oxide and calcium oxide has also been reported [29–31]. However, these works frequently neither detail the treatment conditions nor its effectiveness; also, they appear as not industrially applied. More recently, chromium cake was treated with oxygen in alkaline medium at 433 K to convert all the chromium into an alkali magnesium chromate [32].

The use of products resulting from alkaline hydrolysis has also been studied. The hydrolyzed protein fraction could be used as fatliquour, surfactant and filler for leather manufacture, especially after modification with formaldehyde, glutaraldehyde, acrylic acid, acrylamide derivates, methacrylic acid, polyurethane, enzymes and others [33– 38]. Also, the hydrolyzates are proposed to prepare fertilizers, animal food, surfactants, adhesives and films [39– 43]. Despite alkaline hydrolysis plants at industrial scale are not numerous, an excess of hydrolyzate production is reported, with commercialization difficulties [25, 44]. Thus, research on more

straightforward applications is necessary and one approach is exploring hydrolyzate potential to produce biogas through anaerobic digestion. This three stage biochemical process has been applied to tannery waste water and non-tanned residues and tested to decrease the protein content of chromium cake resulting from alkaline hydrolysis process [45], in which chromium may be recovered namely by incineration, peroxide treatment and others, and used to produce tanning or retanning agents and pigments [46]. However, anaerobic digestion has not been studied for the valorization of the alkaline hydrolizates.

The present work seeks application of one short time wet alkaline relatively mild temperature and pressure treatment to the finished chromium tanned leather scrap; it aims at recovering chromium with maximum organic matrix attack. The effect of NaOH concentration, temperature and time on both chromium and organic matter dis- solution was studied. Anaerobic biodegradability of the resulting liquid phases was assessed.

Materials and Methods

Sample Preparation and Reagents

Six bovine finished chromium-tanned leather samples presenting general properties usual in shoe manufacture were produced using an internal laboratory protocol followed at Centro Tecnológico do Calçado de Portugal (CTCP).

For the characterization of leather as well as pressure- assisted hydrolysis experiments series 1 and 2, and atmospheric pressure hydrolysis tests series 4, the leather samples were shredded to B4 mm using a Pegasil®–Zipor® mill with rotating knives and a 4 mm sieve; following, they were thoroughly homogenized and conditioned in standard laboratory atmosphere at 296 ± 2 K and 50 ± 5 % relative humidity. For the series 3 experiments, the leather samples were cut to 5 cm 9 3 cm, then homogenized and conditioned as above indicated. The 5 cm 9 3 cm size was chosen because it matches better an average scrap size more easily obtainable at industrial plants.

Sodium hydroxide, hydrochloric acid and other reagents used were of analytical grade.

Sample Characterization

The leather samples shredded to B4 mm were chemically characterized regarding pH, total organic carbon, chromium, nitrogen, chlorides and sulfates and forbidden chemicals following standards listed in Table 1 [47–57].

Alkaline Hydrolysis Tests

The pressure-assisted hydrolysis tests were done at least in triplicate using a titanium laboratory autoclave model 4842 from Parr® (Moline, IL, USA) with a 400 mL reaction vessel and no stirring action. The slurries obtained were filtered through glass funnels using Whatman® n. 1 filter paper, either by gravity or under vacuum conditions. The remaining solid residue was washed using distilled water and the washing solution was after added to previously separated solution. These liquids were characterized or frozen at 253 ± 2 K and the residues dried at

373 ± 2 K for characterization.

The experimental plan followed is presented in Table 2. In these experiments the pressure ranged from atmospheric pressure to the maximum of 1.2 ± 0.2 MPa for the tests done at higher temperatures.

In the first experimental series, three screening tests were carried out: (S1.1) 50 g of lab room conditioned leather were mixed with 50 mL of distilled water; (S1.2) 10 g of the same type of leather were mixed with 100 mL of NaOH 0.25 mol/L and at the end, the gas in the reaction vessel was carried out with Helium through 2 gas washing flasks (3–6 bubbles per minute) containing 50 mL of H_2O where, following, chlorides and sulfates were determined; and (S1.3) 5 g of leather dried at 373 ± 2 K were mixed with 100 mL of NaOH 4 mol/L solution and held at 423 K. Again, at the end, the gas in the reaction vessel was carried out with Helium through 3 washing flasks containing, respectively, 150, 100 and 50 mL of H_2SO_4 0.1 mol/L solution. Total nitrogen in these 3 liquid phases was determined and taken as ammonia released in the gases.

In the second experimental series, following the experimental design of a Taguchi orthogonal matrix L9, the objective was analyzing the influence of the NaOH concentration, hydrolysis temperature, hydrolysis holding time and leather to solution ratio on chromium and organic matrix dissolution. After the tests ending and reactor vessel cooling, the slurries were diluted to nearly 1,000 mL with hot distilled water and filtered warm.

In the third experimental series, the aim was tuning and selecting amongst moderate conditions those that favour leather destruction with low cost. With that purpose, samples of 15, 20 and 25 g of leather were mixed with 100 mL of 2, 3 or 4 mol/L NaOH liquid phases and held for 1.5 h at 403, 413 or 423 K. The final slurries were diluted to nearly 1,000 mL and filtered warm.

In the fourth set of tests, the objective was comparing the performance of the tests done previously at 403–423 K with tests done at boiling temperature. Thus, 3 samples with 25 g were refluxed in 250 mL of 1 mol/L NaOH liquid phases for 1, 3 and 5 h at 343 K and at the boiling temperature in the range 370–373 K. The final slurries were filtered warm.

To avoid determining the humidity of the leather sample used in each test, prior to the hydrolysis tests of series 2–4, the leather sample was dried at 373 ± 2 K till constant weight.

Hydrolyzates and Remaining Residues Characterization

The hydrolysis liquid phases and residue materials were characterized according to the standards listed in Table 1. Additionally, in the selected hydrolyzates protein molecular weights (MW) were estimated, by polyacrylamide gel electrophoresis in sodium dodecyl sulfate (SDS-PAGE), using a Major Scientific NM-300 N power source (Saratoga, USA), an electrophoresis system omniPage Mini Vertical from Cleaver Scientific Ld. (Warwickshire, UK) and specific consumables and standards from National Diagnostics (Yorkshire, UK). The gels were prepared and used according consumables provider instructions [58]. Individual gels were precast with stacking gel containing 5 % acrylamide and separating gel with 13.5 % polyacrylamide. For calibration both insulin with 2.5 kDa to 3 kDa and the standard EC 899 from National Diagnostics [58], which contains a mixture of nine proteins with known MW (10 kDa, 15 kDa, 25 kDa, 35 kDa, 50 kDa, 75 kDa, 100 kDa, 150 kDa and 225 kDa) were used. Hydrolyzates were treated according to the consumables provider instructions [58] and other authors' [59, 60] using 4:1 (v/v) sample:stacking buffer Tris–HCl [10 % (w/v) sodium dodecylsulfate (SDS), 20 % (v/v) glycerol, 5 % (v/v) 2-b-mercaptoethanol and 0.1 % (w/v) bromophenol blue in tris(hydroxymethyl)amino- methane

0.125 mol/L with 0.1 % SDS and pH 6.8 from National Diagnostics Protogel buffer EC 893] heated at 368 K for 10 min. A twelve slot applicator was used to load 20 μL of each sample (at least in triplicate) and the standards. Separation was done at 50–120 V and 50 mA at standard laboratory temperature. Gels were stained with Coomassie Blue R250 (Applichem). The mobility (Rf) of the molecules was measured in mm. The plot of log(MW) versus Rf for the several standards of known MW was used to estimate the MW of the samples.

Qualitative determination of specific aminoacids was also performed in the selected hydrolyzates after derivatization with Edman reagent [61, 62] and separation by high performance liquid chromatography (HPLC) at 254 nm, using a Perkin Elmer system (Series 200 UV/VIS detector and PE LC-250 B pump, Massachusetts, USA), fitted with a C18 HPLC Phenomenex Luna column; and specific consumables and standards for HPLC. For calibration L-aspartic acid, L-glutamic acid, L-glycine, L-histidine, L-serine, and L-proline (all from Fluka) were used.

The selected hydrolyzates were also analyzed by gas chromatography with mass detector (GCMS) using an Agi- lent HP 6890/MSD 5793N from HP®; fitted with a HP-5MS,
30 m × 0.25 mm I.D., 0.5 μm P/N 19091S-133 column; and as carrier gas He at constant flux of 1.2 mL/min. The tests were done in the following conditions: splitless injector at 553 K; oven 1 min at 323 K, followed by heating at 283 K/min till 573 K; transference line at 563 K; and MSD scan mode. The separated compounds were identified using GCMS NIST 1998 library match.

Chromium Recovery Tests

Some preliminary tests were carried out to recover chromium from hydrolyzates in order to evaluate the treatment feasibly and analyze its influence in the liquid phase's biodegradability. The hydrolyzate used in these experiments was obtained in the S3.3 test. Hydrolysate samples were adjusted to pH 2, 3.5 and 4 by adding HCl 12 % at 296 K ± 2 K. The liquids were stirred (approximately 100 ± 5 rpm magnetic stirring) during pH adjustment and then stopped to allow chromium precipitation for 60 min. Following, the liquids were filtered by gravity through Buchner glass funnels using Whatman® n. 1 filter paper and the total chromium analyzed according to Table 1.

Anaerobic Biodegradation Tests

The objective of these tests was to verify if the hydrolyzates obtained, rich in organic matter, might be advantageously valorized by anaerobic digestion, either alone or in co-digestion, to produce biogas. Two approaches were followed: (1) use the hydrolyzate as obtained from hydrolysis; or, (2) after removal of some of its chromium. The inoculum was collected at the waste water anaerobic treatment plant of leather factory ''Curtumes Aveneda'' (Ovar, Portugal). Biodegradability tests were performed using the selected hydrolyzates, as well as gelatine and standard cellulose material Avicel® from Fluka® according to an internal method based in ISO11734:1995 standard [63]. These tests were done at least in triplicate using inoculum sludge with approximately 2 % of total solids. Measurement of biogas and calculations were done using the WTW Oxitop® control measuring based in Süßmuth et al. [64]. In this method, the total coefficient of anaerobic biological degradation, D_t, in percentage, is calculated according to:

$$D_t = 100\frac{nCO_{2,g}; CH_{4,g} + nCO_{2,l}}{nC_{theo}} \qquad (1)$$

where: $nCO_{2;g}$; $CH_{4;g}$—number of moles of carbon dioxide and methane gases formed; $nCO_{2;l}$—number of moles of carbon from carbon dioxide formed in the aqueous phase; and nC_{theo}—theoretical number of moles of carbon in the test liquid phase or standard material.

Results and Discussion

Sample Characteristics

The leather material used has the characteristics that are shown in Table 3. Hexavalent chromium is below the threshold value (3 mg/kg) and the remaining parameters gave results that are in the normal ranges for leather used in footwear

Alkaline Hydrolysis Tests Results

Table 4 summarizes the results obtained in the first series of experiments. The liquid phases obtained are emulsions having several organic compounds plus water that pose hard problems in handling and preparation for chemical analysis. Despite the correct procedures used as, for example, samples early analysis or freezing, the results of chemical analysis present generally a high scatter. The S1.1 test, where leather hydrolysis was at 473 K without NaOH, gave a dark liquid with intense non agreeable odor containing 18 g/L of Cr and 327 g/L of TOC, and a black sediment having 26 % of the original leather weight. Approximately 73 and 66 % of the initial chromium and TOC, respectively, were recovered in that liquid phase.

In the S1.2 test, the leather hydrolyzed at 373 K with 0.25 M NaOH solution gave a brown liquid, hard to filtrate, having 80 % of the TOC and nearly 25 % of solid residue. Thus, these conditions promoted higher TOC recovery than those in the S1.1 test. The biochemical oxygen demand to chemical oxygen demand ratio (BOD/COD) of the liquid is 0.33, meaning that it might have some biodegradability. The gas bubbling liquid phases gave negligible amounts of chlorine as chloride and sulfur as sulfate.

In the S1.3 test, where the temperature and NaOH were increased relatively to the S1.2 test, the filterability was improved and the BOD/COD ratio of 0.71 indicates better biodegradability. The final solid residue contains most of the available chromium in the leather. Less than 2 % of total chromium was determined in the liquid of which around 35 % as hexavalent chromium. After 1 h of hydrolysis treatment, Fig. 1a shows that most of the TOC (≈93 %) and nitrogen (≈91 %) in the leather were dissolved. With longer holding times both the TOC and nitrogen in the hydrolyzate decrease, which indicates that material dissolution is slower than dissolved organics destruction. For the longer holding times, the TOC decrease in the liquid phase is not accompanied by the total inorganic carbon (TIC) increase; this overall carbon decrease in the liquid may be related to CO_2 formation. Regarding nitrogen released, Fig. 1b indicates that only about 0.2 % of the total N in the leather was detected in the gas washing solution.

Table 5 shows the results of the experiments following a Taguchi L9 matrix designed for studying

the effects of NaOH concentration, temperature, time and leather to solution ratio factors on chromium and organic matrix dissolution. These results show that the chromium recovered in the liquid phases was in the range of 8–79 % of total and the leather matrix attack, evaluated through TOC in the solution, was in the range of 69–98 %. Thus, chromium was both in the liquid phase and residue and a relevant part of the organic matter from the leather went to the liquid phase. These results were analyzed using DX6 MFC Application from Stat-Ease Inc. software free version. Analysis of variance shows that the NaOH concentration of the hydrolysis solution is the most influent factor on chromium dissolution and that temperature and time are the most influent factors on the amount of TOC dissolved. Both, chromium and TOC dissolution increase with the increasing level of the factors. Analysis of variance gives to the initial solid to liquid ratio a negligible effect on chromium and TOC recoveries. Thus, to dissolve chromium and disrupt the leather matrix it is recommended to use NaOH concentrations and temperatures in the higher range. However, to fulfill the research objective of per- forming the hydrolysis in relatively mild conditions, the authors defined that the maximum hydrolysis temperature to be evaluate in the final series of tests is 423 K and therefore pressure till 1 MPa.

Figure 2 summarizes the results obtained in the third series of experiments. Despite some variability presented by these results, in some cases leading to incomplete or excessive mass balance for chromium and TOC, that as suggested by other works [65], may be attributed mainly to the heterogeneous composition of liquid phase and leather matrix, they confirm the benefit of increasing NaOH concentration.

The results of the experiments S3.1 to S3.3, in Fig. 2a, show that for maximizing leather matrix dissolution the NaOH 4 mol/L solution is the most effective. Figure 2b depicts that using this solution with higher S:L ratio comparatively to lower S:L ratio lowers the liquid phase pH and increases chromium and TOC concentrations in the hydrolyzate, although decreasing their recoveries in percentage. Figure 2c shows that hydrolysis at 423 K comparatively to lower temperatures gave hydrolyzates with lower pH, increased chromium recovery in the hydrolyzate and decrease the final residue, almost one half of that obtained at 403 K.

The results of these experiments indicate that globally, over 92 % of the organic carbon in the leather went to the liquid phase and at least 80 % of chromium was dissolved, giving hydrolyzates with 3–5 g/L of Cr.

Leather hydrolysis using NaOH 4 mol/L, at 423 K for 1.5 h with S:L of 0.15 (according test S3.3) may be a good compromise for achieving high chromium and leather matrix dissolution at relatively low temperature and pressure, producing a hydrolyzate with approximately 3.8 g/L of Cr and 70 g/L of TOC. Other possible alternatives for this treatment are S:L ratio of 0.2 and temperatures of 403 K or 413 K. Under these three tests conditions, over 98 % of the leather scrap and 88–99 % of Cr are dissolved in the liquid phase. In general, the alkaline hydrolysis treatments reported [4–18], involve multiple sequential steps and longer holding times and fail to achieve this performance. Additionally, these works [4–18] indicate that at the end of the hydrolysis treatment a higher percentage of final solid residue with covalently bounded protein needs to be managed.

The hydrolyzates obtained in the experiments S3.1 to S3.7 were characterized regarding Cr(VI) based in ISO 17075:2007 [49]. Immediately after the reaction no Cr(VI) was detected. However, it was noticed that the liquid phases tend to give Cr(VI) with time. To follow these changes new S3.3, S3.4 and S.3.7 liquid phases were pre- pared which presented no Cr(VI) when analyzed immediately after cooling. Fractions of these liquid phases frozen at 253 ± 2 K and then de-frozen after 24 h, 72 h, 1 week, 1 month, 3 month and 6 month also presented no Cr(VI) immediately

after de-freezing. The 6 month de-frozen liquid phases were then maintained at lab temperature (around 296 ± 2 K) for 1 week and after this time liquid phases S3.3 and S3.4 presented Cr(VI) in the range of 1.4 mg/L to 1.6 mg/L. On the contrary, no Cr(VI) was detected in S3.7 liquid phases obtained at lower temperature (413 K). Cr(III) oxidation to Cr(VI) in S3.3 and S3.4 is probably due to exposure of the liquid phases to UV radiation photo-oxidation helped by alkaline media. It is established that exposure of leather treated with certain alkaline agents promotes the formation of Cr(VI) on heat ageing and particularly with UV exposure [66–69]. Also, studies done with model solutions showed that the hydroxyl radicals (•OH) can oxidize Cr(III) to Cr(VI) in chromium containing tanning solutions [70]. In S3.7 liquid phases, the lower hydrolysis temperature may give a contribution to prevent this conversion.

Figure 3 presents the results from the fourth set of experiments. Chromium recovered in the hydrolyzate is in the range of 60–80 % of total and at least about 85 % of the matrix total organic carbon went into the liquid phase. These results are in line with those obtained by other authors [18], which obtained near 18 % (w/w) of solid residue by boiling shavings till 120 min; even thought, as expected the treatment of retained and finished leather is less efficient. Also, the results obtained in the present study confirm that extending the batch residence time has a small effect on reducing the mass of solid residue; however chromium dissolution proceeds with time. Globally the results obtained indicate that despite the relatively mild temperatures used in the third set of experiments, chromium dissolution is higher and the final solid residue is much less, than that obtained by alkaline treatments at boiling temperature or alkaline enzymatic hydrolysis, both applying longer treatment times [4–18]. As reported by other authors [17] that compared chromium tanned shavings alkaline hydrolysis (CaO, MgO or NaOH at 371 K for 3, 6 and 24 h), enzymatic hydrolysis and multi-step alkali hydrolysis, basifiers are more efficient than the enzymes and the higher protein yields are obtained with NaOH, thus reaching 72 % after 24 h hydrolysis.

Figure 4 presents de estimated protein molecular weights (MW) of selected hydrolyzates. Samples S3.3, S3.4 and S3.7, obtained at 413–423 K with holding times of 1.5 h gave similar results and contain molecules with estimated MW mostly around 10 KDa and 15 KDa and till 35 KDa.

From samples S4.1, S4.2, S4.3 and S4.4, those obtained with longer holding times (up to 5 h) and higher temperature (till boiling) resulted in molecules with lower estimated MW and higher dispersion of MW, however always above 25 KDa and till 200 ± 10 KDa. As indicated by other authors [71], there is a MW dependence on temperature and batch residence time.

The effect of temperature and pressure on the molecular mass of collagen hydrolyzates is evident, even at the low batch reaction times, indicating the process as having interest especially for applications requiring hydrolyzates with lower MW and allowing some chromium. Some authors [71], reported the opportunity of using low MW collagen chromium ‘‘free’’ hydrolyzates as additives in foliar nutritive fluids. Other authors [25], due to the difficulty of marketing the hydrolysis resulting by-products, reported the need of reducing the molecular weight of hydrolyzates obtained by alkaline enzymatic hydrolysis at industrial scale to facilitate the application as plant biostimulators. More recently, potential methods for molecular weigh control of collagen hydrolyzates that may favor the specific utilizations of leather wastes were reported [38].

Qualitative HPLC analysis of some of the specific acids and aminoacids more abundant in leather, as aspartic acid, glutamic acid, glycine, serine, histidine and L-proline, in samples from tests S3.3, S3.4, S3.7, S4.1, S4.2, S4.3 and S4.4, indicated the hydrolysates as containing glycine and L-

proline. Also, serine was detected in all the samples from alkaline hydrolyzates obtained at atmospheric pressure. Thus, these treatments may break the proteins chains till the aminoacids level of magnitude.

Samples from tests S3.3 and S3.4 were analyzed by gas chromatography with mass detector (GC–MS). The extracted spectra obtained and the corresponding main structures are presented in Fig. 5. The global mass spectrum of the more relevant picks indicates the two samples as relatively similar. The molecular ions (m/z) more frequent in the chromatogram and with higher relative abundance have molecular mass of 70, 80 and 154. The main chemical structures identified include alkyl group and chains; single, double or triple car- bon–carbon bonds; carbonyl group; nitrogen-carbon bonds; amides; and rings containing non-carbon atoms. NIST 1998 data base suggests the presence of amides, amines, alkenes ($C_{10}H_{20}$), fatty alcohols ($C_{11}H_{24}O$, $C_{12}H_{26}O$, $C_{13}H_{28}O$), esters (methyl, octyl), and proline related compounds, among others. Sample S3.3 after derivatization for aminoacids analysis by HPLC, was also analyzed by GC–MS. NIST 1998 data base suggests the presence of small peptides, namely tripeptide l-alanyl-glycyl-glycine, esters, histidine and pro- line derivates, among others.

Chromium Precipitation Results

Hydrolyzate from test S3.3 acidified to pH 2, 3.5 and 4 gave 24, 27 and 22 % chromium precipitation, respectively. However, chromium and organic matter precipitation occur simultaneously. Thus, these results are useful
only to evaluate the potential effect of chromium in the anaerobic biodegradability of the hydrolyzate.

Biodegradability Tests Results

In the test conditions studied the standard cellulose material coefficient of total anaerobic biological degradation, D_t, as defined by the expression (1), was 70 ± 5 % in 90 days. In the same conditions culinary gelatin presented $D_t = 90 \pm 5$ %. The hydrolyzates from experiments S2.3, S2.5, S2.6, S2.8 and S2.9, obtained at 423 K or 453 K having, respectively, (1.3 ± 0.7) g Cr/L, (6.3 ± 0.6) g Cr/L, (0.3 ± 0.0) g Cr/L, (0.2 ± 0.0) g Cr/L and (2.6 ± 0.1) g Cr/L, gave D_t in the range of 15 % to 45 %, as presented in Table 5. The liquid phases S2.6 and S2.8 with lower chromium content gave the highest D_t. The liquid phases from the third set of experiments had chromium in the range of 3 g/L to 5 g/L and gave D_t in the range of 20 % to 30 %, as reported in Fig. 2. The biodegradability tests on the S3.3 hydrolyzate gave $D_t = 25 \pm 5$ %. S3.3 was also tested after chromium precipitation at pH 3.5 giving $D_t = 30 \pm 5$ %. Figure 3 depicting the results of the fourth set of experiments shows D in the range of 20–30 % and the highest D assigned to the solution S4.2 with less total chromium. Therefore, despite the variability of the results, one may conclude the effect of the hydrolysis conditions on the total inherent anaerobic biodegradability of the hydrolyzates tested is small, perhaps because the method chosen to evaluate that characteristic is not much sensible to their differences. As referred by other authors [2], chromium concentration in the hydrolyzate may have any or little influence on its anaerobic degradation, probably because the neutral pH imposed in the biodegradation test promotes Cr(III) hydroxide precipitation. Anyway, there is a tendency to have higher coefficients of total anaerobic biological degradation, D_t, associated to hydrolyzates with less chromium.

Conclusions

Chromium tanned leather scrap from footwear manufacturing can be hydrolysed at 423 K for 1.5 h with NaOH 4 mol/L and S:L (g:mL) ratio of 0.15 leading to almost complete leather and chromium dissolution. Chromium is almost all trivalent in the alkaline hydrolyzates analysed; however, a small fraction of it may oxidize to the hexa- valent state when the alkaline medium is exposed to the ambient conditions. Acidification of the hydrolyzates stabilizes chromium in trivalent state and precipitates part of it as well as part of the organic matter present. Most of the hydrolyzates obtained show anaerobic biodegradability in the range of 20–30 %. The chromium concentration and alkalinity of hydrolysates may consider their use without any treatment during leather tanning process for pH adjustment. The influence of hydrolysis under pressure above atmospheric and below 1 MPa, on the molecular mass of the organic compounds in the hydrolyzates prove to be relevant, opening some interest for applications of the hydrolizates with some chromium and organics with lower MW.

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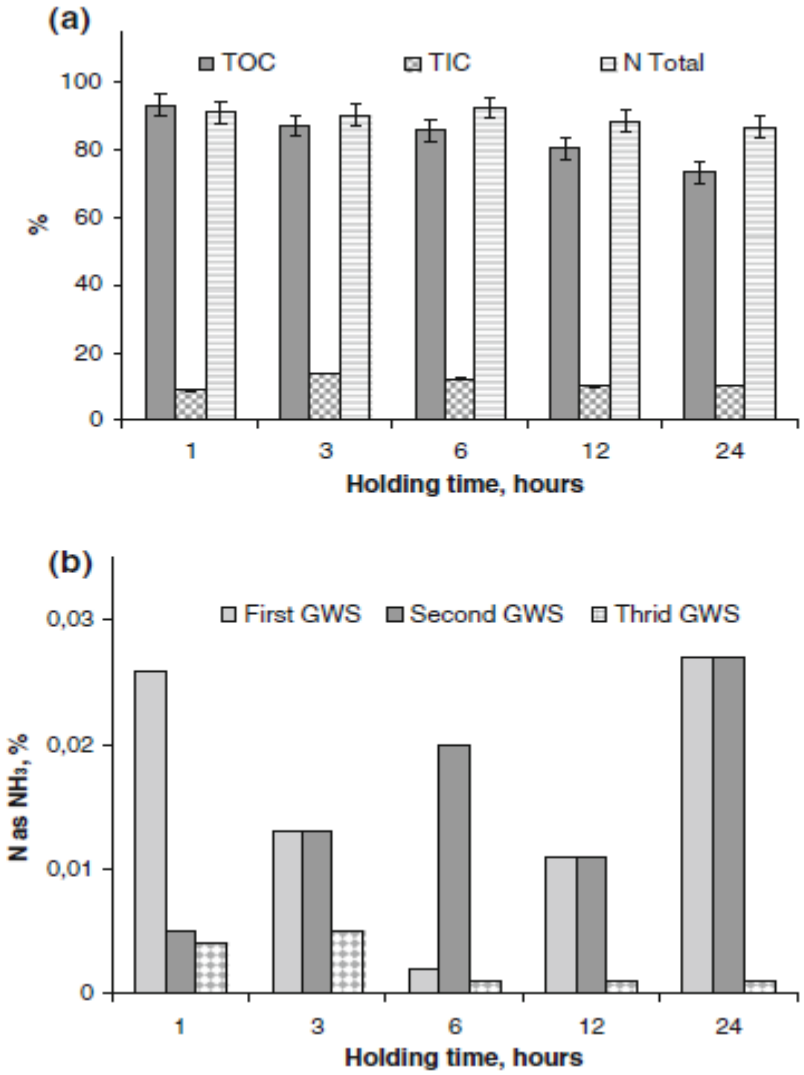


Fig. 1 Results of the S1.3 test—leather pressure hydrolysis: a hydrolysis solutions characteristics; and b nitrogen released detected in the 1st, 2nd and 3rd gas washing solution. GWS gas washing solution.

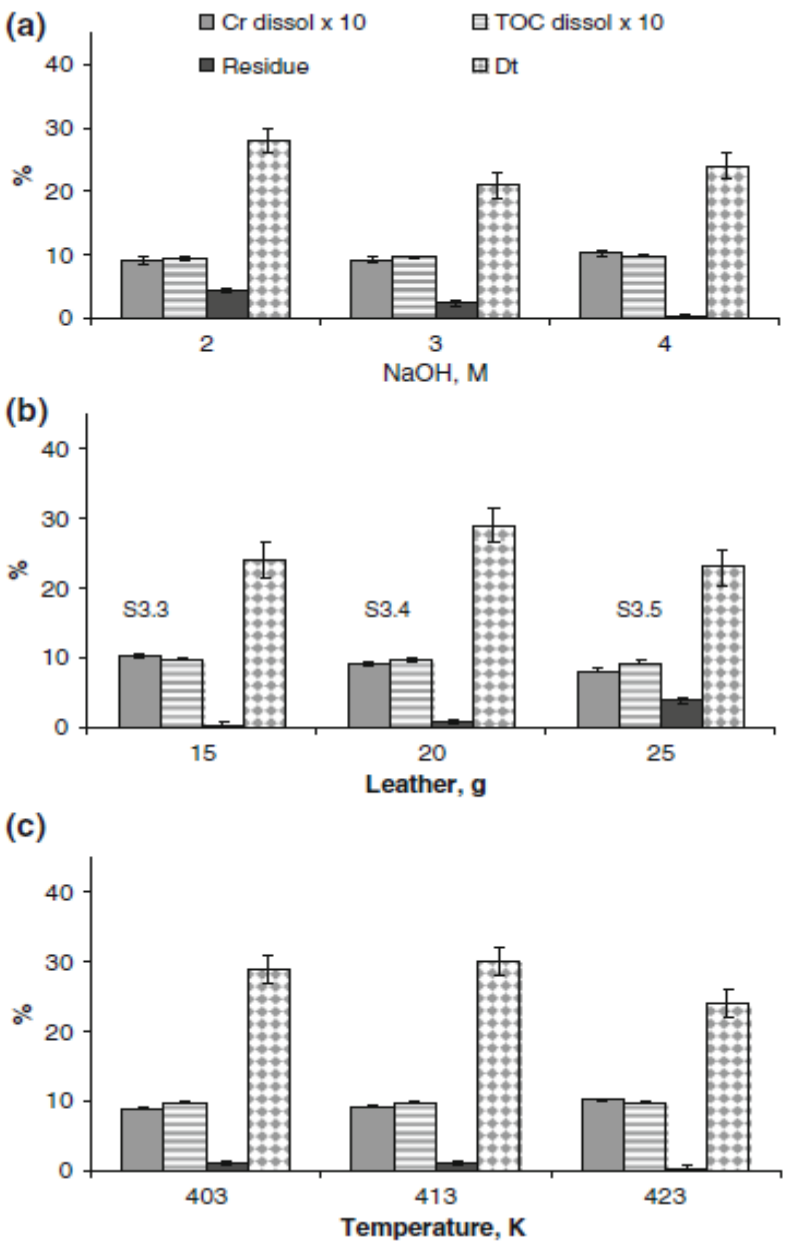


Fig. 2 Results of the third set of tests—leather pressure hydrolysis optimization: a NaOH concentration levels (tests S3.1, S3.2 and S3.3); b leather mass levels (tests S3.3, S3.4 and S3.5); and c temperature levels (tests S3.6, S3.7 and S3.3). dissol—dissolved in the hydrolysis solution; Dt—total anaerobic biodegradability.

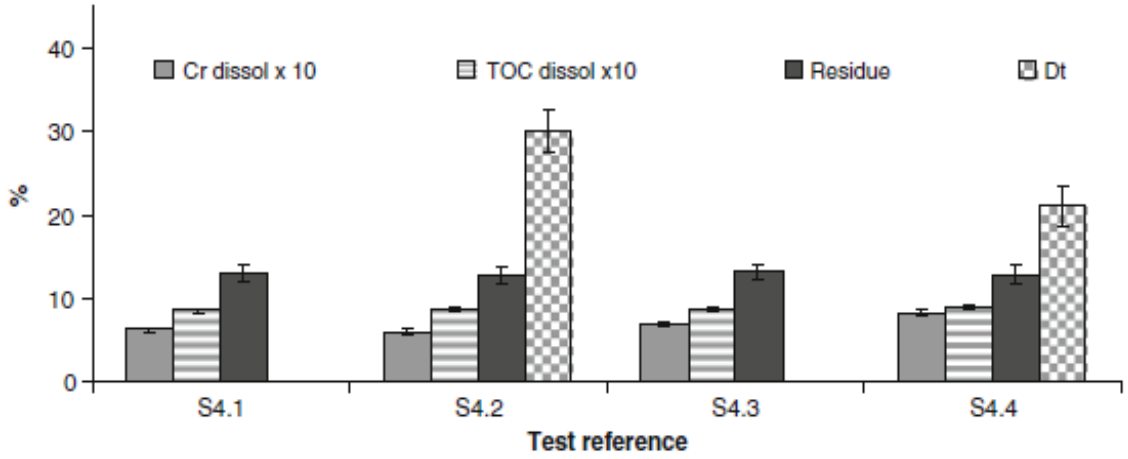


Fig. 3 Fourth set of tests results—leather atmospheric pressure hydrolysis. dissol—dissolved in the hydrolysis solution; Dt—total anaerobic biodegradability

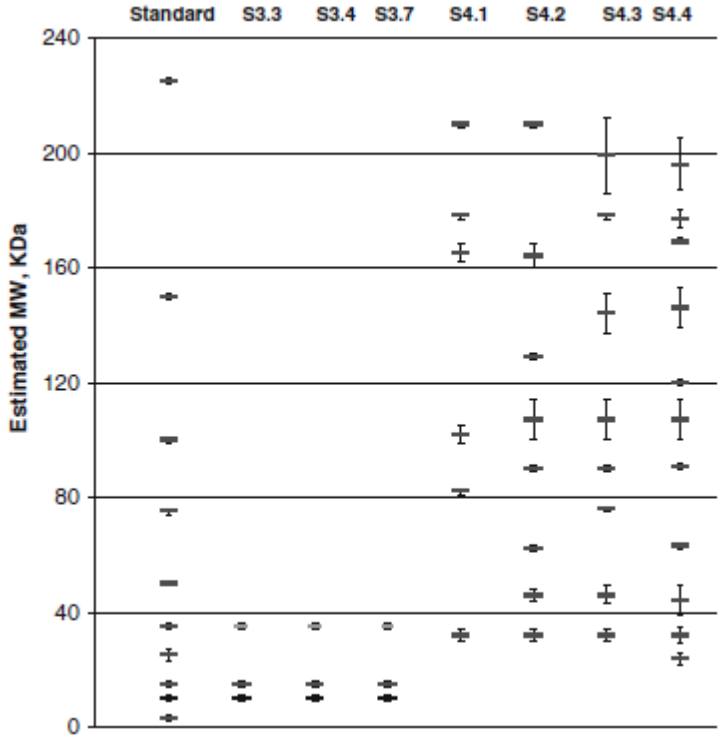
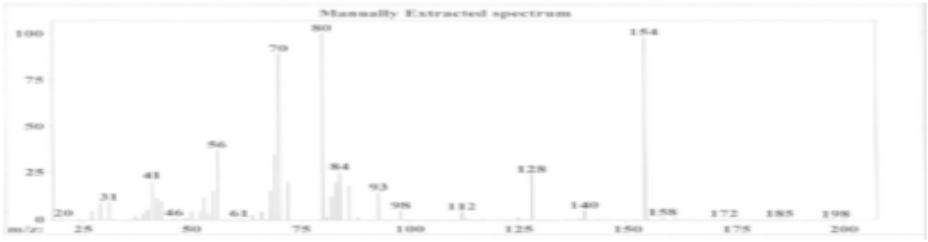
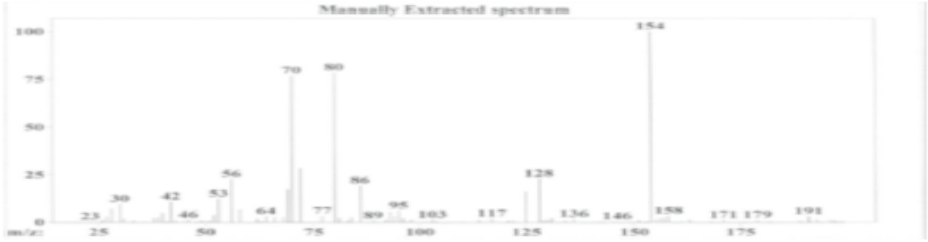


Fig. 4 Estimated molecular weight distribution of organics in the selected hydrolyzates

Sample	Manually extracted GC–MS spectrum	m/z - relative abundance
S3.3		41 – 20 56 – 37 70 ± 2 – 143 82 ± 2 – 145 128 – 24 154 – 98
S3.4		56 – 22 70 ± 3 – 122 83 ± 3 – 97 127 ± 2 – 39 154 – 100

Main structures identified

CH2, methylene group and chain	CH&O , contains only carbon , hydrogen and oxygen
-CH2/3-, methylene or methyl group (chain)	CH2-CH20H, methylene primary alcohol
CH2/3, primary or secondary saturated carbon	>C=O, carbonyl group; C=O, ring carbonyl, esters
(CH2)3-ch, trimethylene linkage	N-C, nitrogen-carbon single bond
CH2-CH2/3, ethyl or dimethylene group (chain)	N-trisub, saturated nitrogen III; N.-sat, saturated nitrogen atom in ring
CH2-CH2-CH2/3, trimethylene group (chain)	C=ONH, amide
CH3, methyl; methyl bonded to carbon	amide, >N(C=O)
C3+-alkyl, methylene attached to saturated C-atoms	R-Amide, >N(C=O)-C(saturated)
C2H5/CH2CH2, primary or secondary ethyllinkage	rings present, ring containing non-carbon atom(s);
C5+, n-alkyl with 5 or more carbon atoms	ring containing at least one heteroatom
C11+, n-alkyl with 11 or more carbon atoms	no aromatic rings present
CC , contains a single, double or triple carbon-carbon bond; carbon-carbon double bond chain and ring	

Fig. 5 Samples S3.3 and S3.4 manually extracted GC–MS spectrum, molecular ions (m/z) relative abundance and main structures identified

Table 1 Chemical methods to characterize leather samples, hydrolysis solutions, gases collecting solutions and final solid residues [47–57]

Parameter	Method
Leather and final residues	
pH	ISO 4045:2008 [47]
Total organic carbon	EN 13137:2001 [48]
Hexavalent chromium	ISO 17075:2007 [49]
Azo colorants	ISO 17234-1:2010 [50]
Pentachlorophenol	ISO 17070:2006 [51]
Volatile matter	ISO 4684:2005 [52]
Nitrogen and hide substance	ASTM D 2868-96(2001) [53]
Total Cr	Digestion US EPA 3050B:1996 and AAS [54]
Chlorides	ASTM D 4653-87(2009) [55]
Sulphates	ASTM D 4655-95(2006) [56]
Hydrolysis and gas collecting solutions	
pH	ISO 4045:2008 [47]
Total Cr, Cr(VI)	US EPA 3050B:1996 and AAS [54], ISO 17075:2007 [49]
Total organic and inorganic carbon	EN 13137:2001 [48]
Chemical and biochemical oxygen demand, chlorides, sulphates, ammonia	Standard methods for examination of waters and wastewater: 1997, 1998 and 2003 [57]

AAS atomic absorption spectroscopy

Table 2. Experimental plan and tests conditions.

Set series	Test	Solution	Temperature (K)	Holding time (h)	Solid to liquid ratio
First preliminary tests	S1.1	H_2O	473	1	1:1
	S1.2	NaOH 0.25 M	373	1	1:10
	S1.3	NaOH 4 M	423	1, 3, 6, 12, 24	1:20
Second Taguchi L9 matrix	S2.1	NaOH 1 M	393	0.5	1:2.5
	S2.2	NaOH 1 M	423	1.5	1:6.25
	S2.3	NaOH 1 M	453	2.5	1:10
	S2.4	NaOH 2.5 M	393	1.5	1:10
	S2.5	NaOH 2.5 M	423	2.5	1:2.5
	S2.6	NaOH 2.5 M	453	0.5	1:6.25
	S2.7	NaOH 4 M	393	2.5	1:6.25
	S2.8	NaOH 4 M	423	0.5	1:10
	S2.9	NaOH 4 M	453	1.5	1:2.5
Third optimization	S3.1	NaOH 2 M	423	1.5	1:6.6(7)
	S3.2	NaOH 3 M	423	1.5	1:6.6(7)
	S3.3	NaOH 4 M	423	1.5	1:6.6(7)
	S3.4	NaOH 4 M	423	1.5	1:5
	S3.5	NaOH 4 M	423	1.5	1:4
	S3.6	NaOH 4 M	403	1.5	1:6.6(7)
	S3.7	NaOH 4 M	413	1.5	1:6.6(7)
Fourth comparison	S4.1	NaOH 1 M	343	5	1:10
	S4.2	NaOH 1 M	Boiling	1	1:10
	S4.3	NaOH 1 M	Boiling	3	1:10
	S4.4	NaOH 1 M	Boiling	5	1:10

Table 3 Characteristics of leather sample

Parameter	Result
pH	3.8 ± 0.1
Total Cr (g/kg)	24.8 ± 0.2 (~2.5 %)
TOC (%)	49.5 ± 0.3
Chromium (VI) (mg/kg)	<3
Azo colorants (mg/kg)	<30
Pentachlorophenol (mg/kg)	<5
Chlorides (g/kg)	1.4 ± 0.1 (~0.1 %)
Sulphates (mg/kg)	34.2 ± 1.4 (~3.4 %)
Nitrogen (%)	11.7 ± 0.2
Hide substance (%)	65.9 ± 0.7

Table 4 Results from the first set of tests

Hydrolysis solution						Solid residue	
Cr total (%)		TOC (%)				Weight (% of initial)	
Test S1.1							
73.4 ± 3.1		66.2 ± 2.6				26.4 ± 1.2	
Hydrolysis solution						Gas washing solution	
Cr total (%)	Cr(VI) (%)	TOC (%)	N total (%)	BOD (g/L)	COD (g/L)	Chlorides (%)	Sulphates (%)
Test S1.2							
72.5 ± 2.2	1.84 ± 0.3	79.9 ± 2.3	81.9 ± 1.9	37.5 ± 1.1	112.9 ± 1.5	<0.001	<0.008
Solution after 24 h				Solid residue after 24 h reaction			
Cr total (%)	Cr(VI) (%)	BOD (g/L)	COD (g/L)	Weight (% of initial)		Cr total (%)	TOC (%)
Test S1.3							
1.2 ± 0.2	0.4 ± 0.1	21.6 ± 0.1	30.5 ± 0.2	16.0 ± 0.2		98,1 ± 2,0	5,7 ± 1,0

Weight, %—refers to the % of the initial weight

Table 5 Results from the second set of tests—Taguchi orthogonal matrix L9

Test	Cr dissol (%)	TOC dissol (%)	Residue (%)	D_t, (%)
S2.1	48.8 ± 6.1	69.4 ± 8.1	28.0 ± 2.3	–
S2.2	78.6 ± 1.4	96.6 ± 2.3	0.7 ± 0.1	–
S2.3	42.2 ± 0.9	89.1 ± 2.7	4.7 ± 1.4	15–25
S2.4	22.6 ± 4.2	98.3 ± 3.1	0.7 ± 2.6	–
S2.5	63.0 ± 6.5	81.4 ± 8.8	4.4 ± 2.3	15–25
S2.6	8.0 ± 0.6	89.2 ± 2.3	9.0 ± 0.1	25–35
S2.7	19.0 ± 6.5	74.4 ± 4.6	19.5 ± 4.2	–
S2.8	8.0 ± 0.1	88.8 ± 2.6	10.3 ± 1.6	35–45
S2.9	25.8 ± 1.4	88.8 ± 0.1	9.5 ± 0.5	20–30

Dissol—dissolved in the hydrolysis solution; D_t—total anaerobic biodegradability