Ultrasound-Assisted Extraction of Cr from Residual Tannery Leather: Feasibility of Ethylenediaminetetraacetic Acid as the Extraction Solution

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ABSTRACT: In this work, the use of ultrasound energy for chromium removal from residual tannery leather was investigated. The following parameters were evaluated: complexation temperature (60−90 °C), chromium/complexant molar ratio (1:0 to 1:6), complexation time (30−120 min), washing steps (1−14), washing temperature (25−80 °C), and washing time (1−10 min). For all evaluated conditions, chromium removal was monitored by flame atomic absorption spectrometry. The residual tannery leather after different extraction strategies were characterized using a scanning electron microscopy. For the proposed method, the optimized conditions were: 3 g of residual tannery leather to be treated, 100 mL of extraction solution (chromium/complexant molar ratio of 1:3), at 80 °C and 30 min of sonication. To complete the chromium removal, only five washing cycles (50 mL of water at 50 °C) of 3 min were required. Using these conditions, a chromium removal higher than 98% was achieved. Under the same reaction conditions, the results were compared with mechanical stirring (100 rpm), which allowed observing the significant effects of ultrasound for chromium removal. Comparing to the conventional method, the total time of the process (including extraction and washing steps) was decreased from 150 to 45 min and the water volume for the washing was reduced from 450 to 250 mL. Therefore, the proposed ultrasound-assisted process can be considered as a suitable alternative for chromium removal from residual tannery leather.

1. INTRODUCTION

Chromium is an element introduced into the environment mainly by industrial activity, such as pigments manufacture and leather tanning.1,2 Although Cr has been used in several industrial applications, it is neurotoxic and a potential problem for the environment and human health.2−4 On this aspect, the maximum concentration of Cr(VI) and Cr(III) allowed in industrial effluents and wastes in several countries started to be strictly regulated. In Brazil, the maximum limits for residual water are 0.1 and 1.0 mg L−1 to Cr(VI) and Cr(III), respectively.5

Among the industrial processes, Cr(III) has been widely used in wet-blue tanning by diffusion through the pores of the leather.1,2 Then, Cr reacts with carboxyl groups from collagen, forming inter or intra molecular crosslinks, increasing the physical and chemical resistance of the material.3,4 After the process, the residual tannery leather presents a high Cr concentration, low compaction ability, and low density, being classified as a dangerous waste and requiring the disposal in industrial landfill.6,7 The expensive costs of land disposal associated with the decrease in the number of disposal sites have led to an increased search for alternative treatments for these residues.8,9

A few studies have proposed the reuse of these residues without Cr removal, which can be used for dyes adsorption (e.g., drimarem red, cibacrone yellow and procion blue).10,11 In these cases, the adsorption efficiency using these residues has been successfully compared to the reference method using active coal.10,11

Despite its high toxicity, after Cr removal, the residual tannery leather can be used in alternative processes. Some authors have reported the use of this material for the production of animal feed and as mineral source for plants nutrition.12−14 Several applications such as immobilization of residual leather in building blocks, blends manufacture, production of antistatic floor, and membranes replacement can be highlighted for engineering applications.15,16

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The main limitation for the reuse of residual tannery leather is the difficulty of Cr extraction. Some alternatives have been proposed, such as the use of hydroxamic acids and enzymatic hydrolysis.\textsuperscript{17–20} However, the use of hydroxamic acids requires a long time (36 h) to achieve an efficient extraction (more than 85%).\textsuperscript{17} In addition, the process based on enzymatic hydrolysis is limited by the formation of metabolic inhibitory products, combined with the high acquisition cost of pure enzymes.\textsuperscript{18} Moreover, these processes generate significant leather degradation, reducing the yield and the quality of raw materials.\textsuperscript{17–20} In this sense, the development of alternative methods for Cr extraction from residual tannery leather are needed, making possible the increasing of waste reuse.

Ultrasound is considered a suitable approach for the improvement of several processes, including extraction, oxidation, desulfurization, adsorption, among others.\textsuperscript{21–30} When ultrasound is applied in extraction processes in a liquid medium containing solids, bubbles can be formed with further collapse (cavitation) in the liquid–solid interface, increasing the transport rates of extraction solution as well as the surface area of the substrate.\textsuperscript{31,32} This more effective contact between liquid and solid phases can be attributed to the micro-jets formed during the bubble collapse, which increase the leaching properties of the extraction solution.\textsuperscript{33,34} In addition, some radical species can be formed during the cavitation, affecting the extraction conditions as well as the stability of some compounds.\textsuperscript{35–37} Among the advantages of ultrasound-assisted extraction (UAE), comparing to the conventional extraction methods, the reduction of extraction time, low reagent consumption, and milder temperature can be highlighted.\textsuperscript{36,37} The challenges in the extraction procedures are associated with the high initial cost and the scaling difficulties in industrial flow.

Despite several advantages of using ultrasound in chemical processes, it has been used mainly for the pretreatment of tannery leather.\textsuperscript{7} In this case, the ultrasound application during leather tanning improves the Cr uptake and reduces significantly the shrinkage.\textsuperscript{6} However, no studies were found in the literature about the effect of ultrasound on Cr extraction from tannery residual leather.

Taking into account the feasibility of ultrasound for extraction of several compounds from different materials, Cr removal from residual tannery leather using ultrasound energy was investigated. Several reaction conditions, such as complexation temperature, Cr/ethylenediaminetetraacetic acid (EDTA) molar ratio, complexation time, washing steps, washing temperature, and washing time were evaluated. Additionally, experiments using conventional extraction (silent condition) were optimized for comparison of extraction efficiency. Chromium determination was performed by flame atomic absorption spectrometry (FAAS). In addition, after applying the UAE process and conventional extraction, the treated tannery leather was characterized by scanning electron microscopy (SEM).

2. RESULTS AND DISCUSSION

2.1. Chromium Determination in Residual Tannery Leather by FAAS. The assessment of total element concentration (e.g., Cr) is an important parameter for the development of extraction protocols.\textsuperscript{36,37} The residual tannery leather was digested in a heating block for subsequent Cr determination. Chromium was determined by FAAS and concentration was 25 285 ± 94 mg kg\textsuperscript{-1}.

2.2. Evaluation of Cr/EDTA Molar Ratio for Conventional Extraction. EDTA is a well-known complexant for several elements, including Cr and has been widely used in extraction methods. The reaction between EDTA and Cr provides the formation of a water-soluble complex that might be extracted from residual tannery leather applying washing cycles. In this sense, the Cr/EDTA molar ratio was evaluated from 1:1 to 1:6. In this study, 100 mL of extraction solution and 3 g of residual tannery leather were stirred for 120 min at 70 °C were employed, followed by 14 washing steps with 50 mL of water at 25 °C and 10 min. The results are shown in Figure 1.

![Figure 1](https://example.com/image1.png)

Figure 1. Influence of the Cr/EDTA molar ratio on the Cr removal by conventional extraction (n = 3). Conditions: 100 mL of extraction solution and 3 g of residual tannery leather stirred for 120 min at 70 °C, followed by 14 washing steps with 50 mL water at 25 °C and 10 min.

For the Cr/EDTA molar ratio of 1:1, Cr removal was 81.4 ± 0.7%. When 1:3 and 1:6 were evaluated, Cr removal was slightly increased to 89.6 ± 0.6 and 90.0 ± 0.5%, respectively. Taking into account that no significant difference (Tukey–Kramer) was observed for the molar ratios 1:3 and 1:6, the molar ratio 1:3 was chosen for subsequent experiments.

2.3. Evaluation of Washing Steps for Conventional Extraction. As previously mentioned, washing steps are necessary for Cr removal, taking into account that Cr/EDTA complex is soluble in the aqueous phase. In this way, up to 14 washing cycles were evaluated. In this study, 100 mL of extraction solution (molar ratio 1:3) and 3 g of residual tannery leather were stirred for 120 min at 70 °C. The water volume, time, and temperature for each washing step were kept constant as 50 mL, 10 min and 25 °C, respectively. The washing time was also evaluated (1, 3, 5 and 10 min), but better results were achieved using 10 min. The results for the experiments of washing are shown in Figure 2.

As can be seen in Figure 2, using 9 washing cycles, the efficiency of Cr removal (89.6 ± 0.6%) did not increase significantly, and the residual Cr in tannery leather was 7.4 ± 0.6 mg kg\textsuperscript{-1}. This residual value is in agreement with the Brazilian Legislation.\textsuperscript{5}

2.4. Evaluation of Temperature and Complexation Time for Conventional Extraction. Considering that Cr/EDTA complexes can be unstable in the aqueous phase because of the ions desolvation (e.g., ion Cr(III) in the
The optimized condition using conventional extraction was 3 g of residual tannery leather, 100 mL of extraction solution (Cr/EDTA molar ratio of 1:3), during 60 min at 80 °C and with 9 washing cycles with 50 mL of water at 25 °C and 10 min. It is important to mention that the overall process (including extraction and washing steps) requires about 150 min to achieve a Cr removal no better than 91%.

2.5. Evaluation of Complexation Time and Acoustic Power of Ultrasound for UAE. After the preliminary experiments, the complexation time (15, 30, and 60 min) for UAE was evaluated. In this study, 3 g of residual tannery leather, 100 mL of extraction solution (molar ratio of 1:3) at 80 °C and 9 washing cycles (50 mL water at 25 °C and 10 min) were used. For experiments using 15, 30, and 60 min, Cr removal was 72.5 ± 0.5, 92.3 ± 0.5, and 92.6 ± 0.4%, respectively. Using 30 min as complexation time, practically the same values for Cr removal were achieved after 60 min of conventional extraction. These results correspond to a reduction of about 50% in the extraction time using UAE.

For the evaluation of the influence of ultrasound in the extraction process, the acoustic power delivered into the system was determined by calorimetry.38,39 Its calculation took into account the variation of temperature, the mass of residual tannery leather, and the specific heat of the solution.38,39 When calorimetry was applied in the ultrasonic bath, the acoustic power was about 2.70 W. On the other hand, the acoustic power for mechanical stirring (100 rpm) was only 0.02 W. Some authors have reported that the use of ultrasound can lead to an increase of energy and mixing, improving the extraction efficiency.36,37 On the basis of these preliminary results, it was supposed that the ultrasound energy can provide an additional energy to increase the Cr removal in the proposed process.

2.6. Influence of Washing Temperature and Time for UAE. During the optimizations, a strong dependence between the washing temperature and Cr removal was observed. In these experiments, 3 g of residual tannery leather, 100 mL of extraction solution (molar ratio 1:3), and 9 washing cycles (10 min each cycle) using 50 mL of water were employed. For the complexation step, ultrasound was applied during 30 min at 80 °C. After, the washing cycles were employed using ultrasound under controlled temperature (25, 50, and 80 °C).

The Cr removal was about 92% after 3 washing cycles using UAE at 25 °C, which was the same efficiency when the conventional process was employed. When 50 °C was evaluated using UAE, the Cr removal was about 98% after 5 washing cycles. Thus, by increasing the temperature (50 °C), it was possible to improve the Cr removal. Considering that 80 °C can start the degradation of residual tannery leather, 50 °C was selected for further experiments.

After optimization of washing temperature (50 °C), the washing time for Cr removal (1, 3, 5, and 10 min) was evaluated. In these experiments, 3 g of residual tannery leather, 100 mL of extraction solution (molar ratio 1:3), and 5 washing cycles assisted by ultrasound with 50 mL of water at 50 °C were employed.

Using 1 min in each washing cycle, the Cr removal was 94.1 ± 0.2%. By increasing the washing time for 3, 5, and 10 min, Cr removal was better but constant at about 98%. Taking into account that no significant difference (Tukey–Kramer) was observed between 3, 5, and 10 min, 3 min was chosen. It is important emphasize that the Cr concentration in the residual tannery leather using these conditions was in agreement to the current legislation.5

Chromium removal using 60 and 120 min at 60 °C was 53.9 ± 1.2 and 55.8 ± 1.2%, respectively. However, when a slight increase in the temperature up to 70 °C was applied, the extraction efficiency using 60 and 120 min was significantly better (81.3 ± 1.2 and 89.6 ± 0.7%, respectively). It is important to mention that no significant difference (Tukey–Kramer) was found between 60 and 120 min at 80 °C (about 91% of Cr removal). Taking into account that the leather starts to degrade at 90 °C, 80 °C was selected as the best temperature.

Figure 2. Influence of the number of washing steps on the Cr removal by conventional extraction (n = 3). Conditions: 3 g of residual tannery leather in 100 mL of extraction solution (Cr/EDTA molar ratio of 1:3). The water volume in each washing was 50 mL, the temperature set at 25 °C, and time of 10 min.

Figure 3. Effect of complexation time and temperature in the conventional extraction (n = 3). Conditions: 3 g of residual tannery leather in 100 mL of extraction solution (molar ratio 1:3) with 9 washing cycles using 50 mL of water at 25 °C and 10 min.
The optimized conditions for Cr removal using ultrasound were 3 g of residual tannery leather, 100 mL of extraction solution (Cr/EDTA ratio molar 1:3), temperature of 80 °C, and 30 min of sonication. To complete the Cr removal, only 5 washing cycles (50 mL of water at 50 °C) of 3 min were required. The overall UAE process (including extraction and washing steps) requires about 45 min to achieve a Cr removal up to 98%.

### 2.7. Characterization of Residual Tannery Leather by SEM

After the optimization of the proposed process, the morphology and structure of residual tannery leather were characterized by SEM. These experiments enable to evaluate if the ultrasound could contribute to the Cr removal, taking into account its chemical and physical effects. Additionally, the energy-dispersive X-ray spectroscopy (EDS) was employed for the qualitative Cr determination. In Figure 4 are shown the micrographs and EDS spectra from residual tannery leather before treatment as well as after conventional extraction and after UAE.

In Figure 4, it is possible to see some substantial differences comparing the treated and untreated residual tannery leather. The untreated leather (Figure 4a) showed particles with microfibrils structures. After the conventional extraction, the morphology of remaining leather was more distinct (Figure 4b) and microfibrils were not observed. After UAE, microfibrils structures were recombined, and the morphology was modified showing small structures as vesicles (Figure 4c).

In addition to the SEM analysis, the EDS spectra showed that the extraction process was successful, evidenced by the identification of Cr only in the untreated leather (Figure 4a). In conventional extraction, peaks of Na and Al were observed (Figure 4b). It is important to mention that some elements as Na and Al were not detected when leather was submitted to the UAE method (Figure 4c).

### 2.8. Complexant Recovery and Its Recycle in the Extraction Process

In order to evaluate the complexant recovery for further recycling in UAE, experiments using acid addition after washing were carried out. These experiments were performed using the residual water (after washing steps) by adding concentrated H₂SO₄ up to complete precipitation of EDTA. The EDTA recovery was calculated by the gravimetric analysis. The EDTA recovery was possible because when in its acidic form, the complex (Cr-EDTA) is unstable, and Cr³⁺ is released into the solution. The EDTA in the acidic form has low solubility (about 0.5 g L⁻¹ at 20 °C) in water and can be

### Table 1. Comparison between the Proposed UAE with Other Processes

| Process          | Time  | Temperature, °C | Extraction Solution                                        | Chromium Removal, % |
|------------------|-------|-----------------|-----------------------------------------------------------|---------------------|
| Acid Extraction  | 36 h  | 30              | 10% oxalic acid                                           | 71                  |
| Acid Extraction  | 6 days| 30              | Concentrated H₂SO₄                                         | 60                  |
| Alkali Extraction| 72 h  | 25              | 0.5 mol L⁻¹ potassium tartrate + 0.25 mol L⁻¹ sodium hydroxide | 95                  |
| UAE, this work   | 45 min| 80              | 3 mol L⁻¹ EDTA solution                                    | 98                  |

![Figure 4. SEM micrographs (magnification of 300 times) obtained for (a) nontreated residual tannery leather; (b) residual tannery leather after conventional extraction; and (c) residual tannery leather after UAE.](image)
easily precipitated. In this work, the EDTA recovery was 97.2 ± 1.3%.

In Table 1, is shown a comparison between the proposed process using ultrasound energy and other systems described in the literature. In the proposed process, the extraction time was significantly decreased when ultrasound was used. It is important to emphasize that a diluted complexant solution was used, and a high extraction efficiency was achieved. In addition, the use of ultrasound energy is in agreement with some green chemistry aspects, once it allows the Cr removal, leather recycling, and complexant recovery.

3. CONCLUSIONS

The UAE was considered an advantageous alternative process for Cr removal from residual tanned leather. It was observed that the ultrasound energy showed better extraction efficiency comparing to mechanical stirring, as well as the reduction of reaction time and water volume (30 and 50%, respectively). The main advantages of UAE comparing to the processes already described are: (i) the use of diluted extraction solutions, (ii) relatively small extraction time, (iii) extraction at atmospheric pressure, (iv) low reagent consumption and (v) EDTA reuse. All these advantages result in the economy of reagents and waste reuse, contributing to the green chemistry aspects.

4. EXPERIMENTAL SECTION

4.1. Instrumentation. The UAE process was performed in an ultrasonic bath (25 kHz), operating at 132 W nominal power (model USC-1800A, UNIQUE, Brazil) at 100% of amplitude. The UAE process was carried out in a glass cylindrical reactor with 5 cm of internal diameter. Temperature was controlled using a circulating water bath (model MCT 110 Plus, Servilab Ltda., Brazil). Experiments for conventional extraction were performed in 100 mL glass beakers using a hot plate, with mechanical stirring (model 752A, Fisatom, Brazil).

For total Cr determination in residual tannery leather, samples were digested in a heating block (MA4004, Marconi, Brazil), equipped with 25 open vessels (capacity of 25 mL). About 0.1 g of sample was digested using 2 mL of concentrated HNO3 and the following heating program was applied: (i) 10 min of ramp up to 115 °C and hold for 120 min at 115 °C and (ii) 20 min for cooling. After cooling, the digests were diluted with ultrapure water up to 25 mL in a volumetric flask for further Cr determination by FAAS. Before determination, samples were filtered through a polytetrafluoroethylene membrane (0.22 µm) and diluted with ultrapure water when necessary.

Chromium determination was performed in a flame atomic absorption spectrometer (model AAS5S, Varian, USA) equipped air/acetone flame was employed. The Cr hollow cathode lamp was operated at 4 mA, the wavelength was set at 357.9 nm, and the spectral band pass was set at 0.8 nm. Signals (absorbance high) were monitored for 3 s.

The residual tannery leather after UAE and conventional extraction, as well as the untreated leather were characterized by SEM (model Sigma 300 VP, Carl Zeiss, Germany) operating in the high vacuum mode with a secondary electron detector for qualitative analysis of images. An energy-dispersive detector for X-ray spectrometry (model Quantax EDS, Bruker, Germany), coupled to the SEM (SEM–EDS) equipment, was used for qualitative analysis of solid residues.

4.2. Reagents, Standards, and Samples. All reagents used in this work were of analytical grade. Deionized water was purified using a Direct-Q UV3 purification system (Millipore, USA), with resistivity of 18.2 µS cm. Stock solution reference of 100 mg L−1 Cr was prepared by dissolution of CrCl3 (Vetec, Brazil) in 5% (m/v) HNO3 solution. Calibration solutions were daily prepared by serial dilution of stock solution in 5% (m/v) HNO3 solution. Ethylenediaminetetraacetic acid (EDTA, purity 99.4%, Sigma–Aldrich, USA), prepared by dissolving a suitable amount in ultrapure water was used for the extraction process. Concentrated HNO3 (65%, Moderna, Brazil) was used for samples digestion, and concentrated H2SO4 (95%, Moderna, Brazil) was used for EDTA recovery after tannery leather treatment.

Residual tannery leather was purchased in a local industry in the Rio Grande do Sul State (Brazil). The feedstock was cut into small pieces with diameters lower than 0.3 cm. Before treatment, the sample was stored in glass flasks at room temperature.

4.3. Methods. Initially, Cr extraction was performed using the conventional process (silent condition). These experiments were carried out in a glass cylindrical reactor with 5 cm of internal diameter. About 3 g of residual tannery leather were transferred to the extraction vessel, 100 mL of extraction solution (EDTA solution) were added and the mixture was submitted to conventional extraction. Then, the removal of Cr/EDTA complex was performed by applying washing cycles with water. After each washing cycle, the solid leather was separated from water, and Cr concentration in aqueous phase was determined by FAAS. The following extraction parameters were evaluated: Cr/EDTA molar ratio (1:1, 1:3, and 1:6), washing steps (1–14 with 50 mL of water) after extraction, complexation temperature (60, 80, and 90 °C), and complexation time (30, 60, and 120 min). All experiments were performed with mechanical stirring at 100 rpm, and the temperature was monitored using a digital thermometer.

UAE was performed under the same conditions applied to the conventional extraction. However, the following parameters were also evaluated: complexation time (15, 30, and 60 min), washing temperature (30, 50, and 80 °C) and washing time (1, 3, 5, and 10 min). It is important to emphasize that the extraction vessel was introduced into the ultrasonic bath considering the position that higher ultrasound intensity (5 cm) and the pH in the extraction step was kept constant (pH = 5.0) in all experiments. The pH 5.0 was chosen for the experiments because of the ability of EDTA as complexing agent. At low pH, the nonionized EDTA predominates and for the complexation to occur, the metal ions must be able to remove the ionizable hydrogens from the EDTA. At high pH, the hydrogens are removed by reaction with hydroxide ions. In this case, there is a “competition” with the hydroxyl groups, and many metal ions can be hydrolyzed and precipitated as hydroxides.

An important feature of UAE and that need to be monitored is the energy input into the system, which was determined by calorimetry according to previous works. This evaluation was performed using 3 g of residual tannery leather and 100 mL of complexant solution, under ultrasound at 100% of amplitude for 20 min. The temperature was monitored using a digital thermometer. Ultrasound power dissipated into the extraction solution was calculated as shown in eq 1.
where \( C_p \) is the heat capacity of water (4.2 J g\(^{-1}\)), \( M \) is the mass of water (g), and \( dT/dt \) is the temperature rise per second. The initial temperature rise was measured at room temperature by using a thermocouple, which was immersed in the extraction solution and was held at the half height of the solution during the extraction.

The residual tannery leather with and without treatment was characterized by SEM. Samples were cut into sections of 10 x 10 mm and mounted on the specimen stub. Metal overlay was not necessary. Samples were observed using SEM—EDS with an accelerating voltage at 8 kV, and the data were collected with a distance of 7.9 mm from the electron source.

Finally, using all the optimized conditions for UAE, the possibility of EDTA recovery in the extraction process was evaluated. These experiments were performed by adding \( \text{H}_2\text{SO}_4 \) to precipitate EDTA-\( \text{H}_2 \).

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