



## Ultrasound-assisted extraction of chromium from tanned leather shavings: A promising continuous flow technology for the treatment of solid waste

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### ABSTRACT

In this work, a continuous flow extraction system assisted by ultrasound (US) was developed for the extraction of Cr(III) from residual tanned leather shavings. US energy was delivered into the system by a tubular applicator (clamp-on tube US applicator). The effect of the US energy was investigated at 20 kHz of frequency and electrical input power of 75, 150, 300 and 600 W. Residence time and temperature profile were also evaluated. It was observed that the internal temperature profile was affected by the presence of US and inverted in comparison with the conditions without US. In this way, the temperature profile generated by the US was reproduced by using electrical resistances in order to compare the obtained results. The US intensity was measured using a hydrophone connected to a sound pressure meter. The use of the US did not alter the dynamic behavior of the system but increased the extraction efficiency when compared to the silent condition. US power above 75 W did not lead to increased extraction efficiency, when the residence time was 30 min. However, when 60 min of residence time were employed, the optimized US power was 150 W, resulting in an extraction efficiency of  $71.7 \pm 0.7\%$ , about 28 % higher when compared to the silent condition in the same temperature and other conditions. The US energy allowed a reduction in processing time and operational temperature when compared to the silent condition with the same temperature profile. The overall energy consumption with US was similar or lower than that observed without US, showing the feasibility of the proposed extraction system.

### 1. Introduction

Tanned leather processing generates high amounts of Cr(III) contaminated solid waste. This element, which is used in tanning industry to improve the resistance and impermeability of leather, can be found in high concentration, around 2 to 3 % Cr(III) in the solid residue. It is estimated that for each ton of initial leather, only 200 kg of tanned leather are produced, generating more than 450 kg of solid waste, and 50 m<sup>3</sup> of wastewater [1]. Several alternatives have been reported to ensure the passivation of these wastes, of which the most applied are hydrolysis, incineration, and landfill disposal. However, the high associated cost and low leather reuse are drawbacks of these treatments [2–6]. Additionally, Cr(III) removal from tanned leather shavings is considered critical to enable leather reuse in other industrial products, such as fertilizers, paints and adhesives.

Many extraction processes of Cr(III) from residual tanned leather

have been developed by using chelating agents [7], organic [8] or inorganic acids [9] and salts [10].

Poulopoulou *et al.* proposed a extraction method that started by soaking the residue with dilute H<sub>2</sub>SO<sub>4</sub> followed by irradiation with a <sup>60</sup>Co source and washing with water. After it, a treatment with NaOH 10 % (w w<sup>-1</sup>) is carried out followed by a treatment with H<sub>2</sub>O<sub>2</sub> at pH ~ 10–11. According to the authors, the mechanism of the removal of Cr (III) from collagen is composed by protein stabilization and subsequent solubilization of Cr(III). The residue presented less than 10 ppm of Cr [11]. Wang *et al.* proposed a substitution-based method for the effective leaching of Cr(III) from the residual tanned leather by using a 2 % (w w<sup>-1</sup>) sodium oxalate solution [10]. Up to 98 % of efficiency was obtained after 300 min of extraction time at 65 °C in a batch system. Malek *et al.* [12] evaluated several organic salts and acids such for their efficiency to separate the chromium from the leather waste. The optimal yield of chromium extraction about 95 % using potassium tartrate after

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72 h of contact time in alkaline conditions.

Ultrasound (US) energy has been shown to be a promising alternative to industrial processes intensification, with many examples of its application, such as desulfurization [13], biomass valorization [14], and extraction procedures [15]. During US propagation, cavitation bubbles, vibrations, crushing, mixings and other comprehensive effects can be observed in the liquid medium [16,17]. The existing literature on the subject demonstrates that the physical and chemical effects caused by US propagation can increase the mass transfer rates of several processes [18].

The ethylenediamine tetraacetic acid (EDTA) chelating agent has been shown as a suitable option for the extraction process, since it forms a stable complex with Cr(III), without degrading the protein fraction. Recently, Popielski *et al.* proposed the use of ultrasound associated with EDTA for complexation and extraction of Cr(III) from residual tanned leather [7]. By using an ultrasonic bath operating at 37 kHz and an EDTA solution (pH = 5), the extraction time was reduced from 150 to 45 min. To ensure complete removal of the Cr(III)-EDTA complex from leather surface, additional washing steps using water were performed. When US was applied during the washing steps, water consumption was reduced from 450 to 250 mL, which represents a reduction of at least 55 % in water consumption, and resulted in extraction efficiencies of up to 98 %. Another study evaluated the use of several acids for the extraction of Cr from this residue in an ultrasonic-assisted batch system [9]. Up to 92 % of efficiency was obtained using 3 mol/L HNO<sub>3</sub> as extracting solution, after 30 min at 30 °C in an ultrasonic bath.

Despite the feasibility of this batch extraction process being demonstrated, the application of this technology for industrial processes requires quantitative prediction of acoustic streaming, power dissipation, mass transfer and acoustic cavitation [16,17,19]. In addition, there are virtually no reports of US application for Cr(III) removal using continuous flow systems, which demonstrates the need for studies evaluating US efficiency for this approach considering that this type of system has higher productivity than batch ones, being more prone to be used industrially to further improve productivity. Thus, the development of continuous flow systems assisted by US is an open topic in development, where a solid-liquid extraction system is still scarce and few examples can be found in the literature.

In this sense, in this work a continuous flow extraction system is proposed, where the effect of US energy on the extraction of Cr(III) from tanned leather shavings was investigated by using a clamp-on tube US applicator and a 3D printed screw conveyor system. The US intensity was measured using a hydrophone connected to a sound pressure meter. The operational characteristics of the system were evaluated keeping the measurement of temperature profiles in the presence of US. The absorbed power and acoustic pressure were measured. The silent condition was established by attaching heating collars to the metallic system walls, in order to reproduce the same temperature profile generated in the presence of US. The effect of residence time and US power on dynamic behavior and extraction efficiency was presented. The Cr(III) concentration profile in the solid phase throughout the system length was determined in the presence of US and compared to the silent condition. The tanned leather shavings were characterized using scanning electron microscopy (SEM), microwave-induced plasma optical emission spectrometry and other techniques before and after the treatment. Additionally, energy consumption was measured and compared among the evaluated conditions.

## 2. Materials and methods

### 2.1. Instrumentation

A SRC UltraWave™ system (Milestone, Italy) was used for the microwave-assisted digestion of leather samples. A microwave-induced plasma optical emission spectrometer (4210 MIP-AES, Agilent Technologies, USA) was used for Cr(III) determination in the digests. The Cr

(III) concentration in the extracting solution was determined using a spectrophotometer (USB2000+, Ocean Optics, USA), equipped with a 2 mm optical path length glass cuvette. The temperature inside of the continuous flow system was measured using a type K thermocouple (3 mm of diameter, 750 mm of length).

Samples and reagents were weighed using an analytical balance (220 g maximum capacity, AY220, Shimadzu, Japan) and a higher capacity electronic balance (10 kg maximum capacity, LC10, Marte, Brazil). Leather samples were dried in an oven before the Cr quantification step (400/2ND, Nova Ética, Brazil). The pH of the extracting solution was measured using a pHmeter (781 pH/Ion Meter, Metrohm, Switzerland) equipped with a glass electrode (6.0262.100, Metrohm, Swiss). The US intensity was measured using a hydrophone (HCT-0310, Onda Corp, USA) connected to a sound pressure meter (MCT-1010, Onda Corp). A clamp wattmeter (ET-4095, Minipa, Brazil) was used for electrical power measurements.

A scanning electron microscope (300VP, Zeiss, Germany) was used to obtain the images before and after the extraction process through a secondary electron detector with variable pressure. A dispersive energy detector for X-ray spectrometry (Quantax EDS, Bruker, Germany), coupled to the system, was used for element quantification during sample scan.

#### 2.1.1. Continuous flow extraction system

The continuous flow extraction system is based on 2" diameter segments connected by tri-clamp fittings. The solid fraction is introduced into the system by a solid dosing unit containing a mass sensor to measure and control the flow rate. Below this unit, the solid and liquid inlet section is connected to the clamp-on tube US applicator (MPI Ultrasonics, Switzerland). The tube consists of a 458 mm long stainless steel tube, with an internal diameter of 47 mm and containing 2" tri-clamp fittings at each end. An US transducer is connected to the tube by a clamp (170 × 110 × 35 mm of dimension) containing a waveguide (140 mm of length, 35 mm of diameter). A shaftless screw conveyor, containing paddles to potentialize mixing, is placed in the center of the tube to transport the solid fraction while the extracting solution is fed to the system in a parallel way. The screw is driven by a stepper motor. A solid and liquid discharge unit is connected to the other end of the US applicator. This unit is positioned at an angle of 45° in relation to the rest of the system. A screw conveyor is used to drive the solids to the outlet port while the liquid phase exits at another port located in this unit. In order to control the temperature of the system, the extracting solution is continuously removed from the system at an additional port located in the discharge section, and reintroduced in the inlet section. A temperature control unit, containing two heating collars, is used to heat the extracting solution to the operational temperature. Most of the parts of the system were 3D-printed, both in poly(acrylonitrile butadiene styrene, ABS) or poly(ethylene cotrimethylene terephthalate, PETT). The whole extracting unit was controlled by a homemade system, composed of Arduino boards, potentiometers, displays, among other components used for selecting the operational parameters of the system, such as residence time ( $\tau$ ) and dosing unit setpoint. The control unit controlled the solid phase flow rate, screw conveyors speed, and the full automation of the system. A peristaltic pump was used to introduce the fresh extracting solution into the system (IPC-N, Ismatec, Switzerland), with a higher capacity pump being used for the recirculation of the extracting solution through the heating control unit (GD150, TMA, Germany).

The US transducers (20 kHz) were driven by an AMMM-1000 W generator (MPI Ultrasonics, Switzerland), which was controlled by the software AMMM Labview (Lab View Run-Time engine 2009 SP1), in which several operational parameters could be set, such as frequency, delivered power, amplitude, among others. This software automatically tracks the impedance matching between the generator and the transducer in order to maximize power transfer, according to process conditions.

## 2.2. Reagents

The extracting solution was prepared by dissolving tetrasodium EDTA (Trilon® B Powder, D-Basf, Germany) in distilled water to obtain the concentration of 14.3 g/L, corresponding to a molar ratio of 3 between tetrasodium EDTA and Cr(III). Hydrochloridric acid (Vetec, Brazil) and sodium hydroxide (Vetec) were used to adjust the pH of the extracting solution to 5.0. Chromium (III) chloride hexahydrate (Dinâmica, Brazil) was used to prepare standard solutions for the spectrometric determination of Cr(III). Concentrated nitric acid (14.4 mol/L, Merck, Germany) was used to digest the leather samples in order to determine residual Cr(III) content.

## 2.3. Samples

Tanned leather shavings were obtained from a leather processing company located in southern Brazil. The sample contained 58.4 % of water and a Cr(III) concentration of  $25.8 \pm 0.5 \text{ mg g}^{-1}$ , on a dry basis. The average particle diameter was 1.12 mm.

## 2.4. Methods

### 2.4.1. Chromium determination in leather samples

Prior to the digestion step, approximately 30 g of the treated leather sample were mixed with 200 mL of distilled water and submitted to five washing steps of five minutes at 70 °C, with 400 rpm of mechanical agitation. Afterwards, samples were dried for 24 h at 105 °C. The digestion step was carried out by transferring 200 mg of dried sample to the digestion vessels along with 6 mL of concentrated nitric acid. The vessels were transferred to the digestion chamber, which was previously filled with 120 mL of water and 5 mL of concentrated nitric acid, followed by pressurization at 40 bar with Ar. The temperature during the heating program was maintained at 250 °C for 10 min, followed by

cooling and depressurization. The digests were transferred to polypropylene flasks and diluted to 50 mL with distilled water.

Chromium concentration in the digests was measured by microwave-induced plasma optical emission spectrometry at 357.868 and 425.433 nm. The measurements were carried out in triplicates with an integration time of 3 s and automatic background correction.

### 2.4.2. Temperature profile measurement

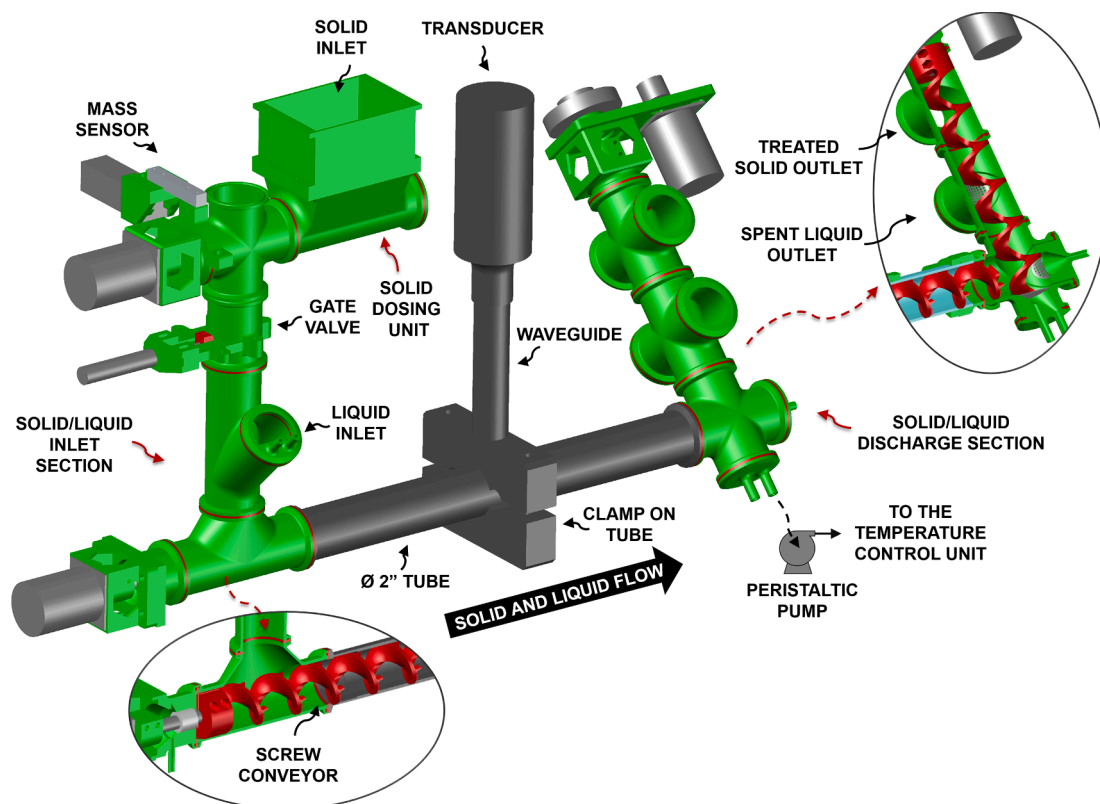
A 3D-printed special adapter was connected to the solid discharge section to allow the introduction of the thermocouple into the system in order to measure its internal temperature profile. The measurement was carried out after reaching the steady state, with the system filled by extracting solution, but without the presence of solid particles. The thermocouple was moved stepwise towards the inlet section and the temperature was registered at every 2.5 cm. The recirculating liquid phase flow rate was set to  $350 \text{ mL min}^{-1}$  and the fresh EDTA extracting solution flow rate was set to  $0.3 \text{ mL min}^{-1}$ .

### 2.4.3. Acoustic pressure determination

Acoustic pressure determination was performed for the input powers of 75, 150, and 300 W, at room temperature. Due to the hydrophone length (27), the US applicator was detached from the system for this procedure, since it would not be possible to reach all internal regions. The applicator was filled with the extracting solution (14.3 g/L, tetrasodium EDTA), the US generator was activated, and the acoustic pressure was recorded in the center of the tube for each evaluated position.

### 2.4.4. Continuous flow extraction

For the continuous flow extraction, the system was initially filled only with the extracting solution (Fig. 1). After reaching the steady state of the inlet and outlet temperatures, the introduction of the solid phase into the system was initiated. The dynamic behavior of the system was assessed by Cr(III) determination in the extracting solution during the



**Fig. 1.** Continuous flow US-assisted extraction system. Components represented in green and red (except for the sealings) were 3D-printed in ABS or PETT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

extraction process. For this procedure, aliquots of the liquid phase were collected at the liquid outlet port of the system and transferred to a glass cuvette for Cr(III) quantification by spectrophotometry at 545 nm [20,21]. Once the steady state was reached (Cr(III) concentration in the extracting solution became constant over time), a sample of the treated solid was collected from the solid outlet port for residual Cr(III) determination. Residence times ( $\tau$ ) ranging from 30 to 120 min were evaluated. For  $\tau = 30$  min, the fresh EDTA flow rate was set at  $41.6 \text{ mL min}^{-1}$ , while for  $\tau = 60$  min, a flow rate of  $20.8 \text{ mL min}^{-1}$  was applied in order to keep the same amount of tetrasodium EDTA for each condition. The average temperature in the experiments was of  $70 \text{ }^\circ\text{C}$ , the liquid phase recirculation flow rate was  $350 \text{ mL min}^{-1}$ , the solid/liquid ratio was 3 %, EDTA concentration was  $14.3 \text{ g L}$  while the EDTA/Cr(III) molar ratio was set at three.

For US-assisted extraction, the generator was switched on during temperature stabilization time, as it affected the heating dynamics of the system. The transducers input electric power was evaluated from 75 to 600 W. The frequency was initially set at 20.9 kHz and the span was set as 1 kHz. The US amplitude and frequency were automatically adjusted by the generator software to keep the power constant over time (amplitude-power mode).

The results for the Cr(III) concentration profile over time were expressed in normalized time, which was calculated according to Eq. (1):

$$\theta = \frac{t}{\tau} \quad (1)$$

Where “ $\theta$ ” is the normalized time, “ $\tau$ ” is the theoretical residence time (set by the screw conveyor speed), and “ $t$ ” is the current time. For example,  $\theta = 1.0$  means that one complete residence time has been elapsed since the beginning of the extraction process.

#### 2.4.5. Solid phase Cr(III) concentration profile

After reaching the steady state, the electronic control of the system was deactivated, the pumps were turned off and the extracting solution was completely drained from the system. Afterwards, the screw conveyor was removed, and the solid contained in each of its sections was carefully collected, dried at  $105 \text{ }^\circ\text{C}$  for 24 h (without a washing step), and submitted to MAD digestion further Cr(III) quantification by MIP-OES. This experiment was carried out under the conditions of 150 W US, 150 W Silent temperature profile, and for the condition without US, at  $70 \text{ }^\circ\text{C}$  and  $\tau = 60$  min.

#### 2.4.6. Solid phase characterization by scanning electron microscopy

Leather samples before and after the extraction process in the optimized extraction condition ( $\tau = 60$  min,  $70 \text{ }^\circ\text{C}$ , 150 W US), were dried in an oven for 2 h at  $60 \text{ }^\circ\text{C}$  for water removal before SEM analysis. A  $30 \text{ }\mu\text{m}$  slit was used for sample imaging and the operating voltage was adjusted to 1 kV. For data acquisition by dispersive energy spectroscopy (EDS), the operational voltage was changed to 20 kV.

### 3. Results and discussion

#### 3.1. Ultrasonic system characteristics and operation

The clamp-on tube US applicator used in this study was selected due to its suitable physical dimensions and fittings, making the flow operation straightforward, as already explored in other works [22,23]. In contrast to probe/horn US applicators, the whole surface of the tube vibrates and transmits energy to the medium, better distributing the acoustic energy in the system (internal area of the applicator of approximately  $676 \text{ cm}^2$ ). Another advantage of the clamp-on tube applicator is that it can operate in closed conditions to prevent contamination, as the processing media is contained entirely inside of the tube [24]. If a higher acoustic power is eventually needed, multiple clamps can be positioned on the tube [24].

The generator used to power the transducer has an advanced electronic control system, which measures the current and electrical voltage applied to the piezoelectrical crystal, as well as the phase between them, allowing to estimate the electrical power consumed by the transducer. Moreover, it allows using a frequency scan, within the operational range of the piezoelectric crystals, in this case  $20 \pm 2 \text{ kHz}$ , in order to determine the best operating frequency (which depends on temperature, type, and amount of material inside of the US applicator). [25] The best frequency corresponds to the one in which the phase between current and voltage is minimal. When the phase is zero, it means that the resonance frequency has been reached and the power that can be transferred from the generator to the transducer is maximized [26].

Another functionality provided by the US generator is related to the control mode, which can be done either by amplitude or by electrical power dissipated by the transducer. The first control mode is similar to that generally found in conventional systems, where the US amplitude is kept constant over time and the power dissipated fluctuates as the medium properties change. In the control mode by the electrical power, the generator automatically varies the amplitude and frequency of operation (to a value closer or farther from the resonance), while keeping the electrical power consumed by the transducer constant over time. [24] To better understand the operation of these control modes, a modification in the control software was performed to allow the logging of the amplitude, power, and frequency throughout the extraction process. The behavior of these parameters can be seen in Fig. 2.

It can be observed that when the control was based on the amplitude (Fig. 2A), the power oscillated significantly over time, while amplitude and frequency remained relatively constant. In the second control mode (Fig. 2B), the power remained relatively constant over time, while amplitude and frequency oscillated constantly. As fluctuations in the power dissipated by the US directly affected the distribution and the temperature profile inside the system, it was more convenient to operate with the second control mode, as it favored the thermal stability of the system. Moreover, the constant movement of the solid and liquid phases through the system caused the absorbed power to naturally fluctuate. Therefore, this control mode could overcome this fluctuation due to continuous power regulation. In this way, this control mode was used during all experiments in which US energy was used, keeping the electric input power constant over time. It is important to note that the measured and controlled power by the generator refers to the electrical power consumed by the piezoelectric transducers and not the power actually absorbed by the liquid phase, which is probably lower due to energy dissipation in other ways, such as by heat generation [25].

#### 3.2. Effect of US on the temperature profile

Experiments were carried out to identify the thermal behavior of the system when US energy was being dissipated in the medium. In the first study, when US energy was not applied, it was observed that the temperature profile of the system was dependent on the liquid phase recirculation flow rate (used to allow temperature control), being  $350 \text{ mL min}^{-1}$  the optimal flow rate. For the evaluation of the influence of US power on the temperature profiles, the internal temperature profiles were measured as a function of the applied electric power in the US transducer. The obtained results are shown in Fig. 3A.

It is possible to observe a linear increase in the temperature of the liquid phase in the region between 0.2 and 0.8 of the US applicator tube position, where the US energy was dissipated most intensely. It is also possible to observe that the temperature profile showed an inverted behavior in relation to the condition without US, where the outlet temperature of the liquid phase of the system was lower than the inlet temperature. This is possibly due to the dissipated US energy in the liquid phase, which is higher than the energy lost through the walls of the system, leading to an increase in temperature towards the discharge section. As the power was increased, the greater was the difference between the inlet and outlet temperatures of the liquid phase. For a power

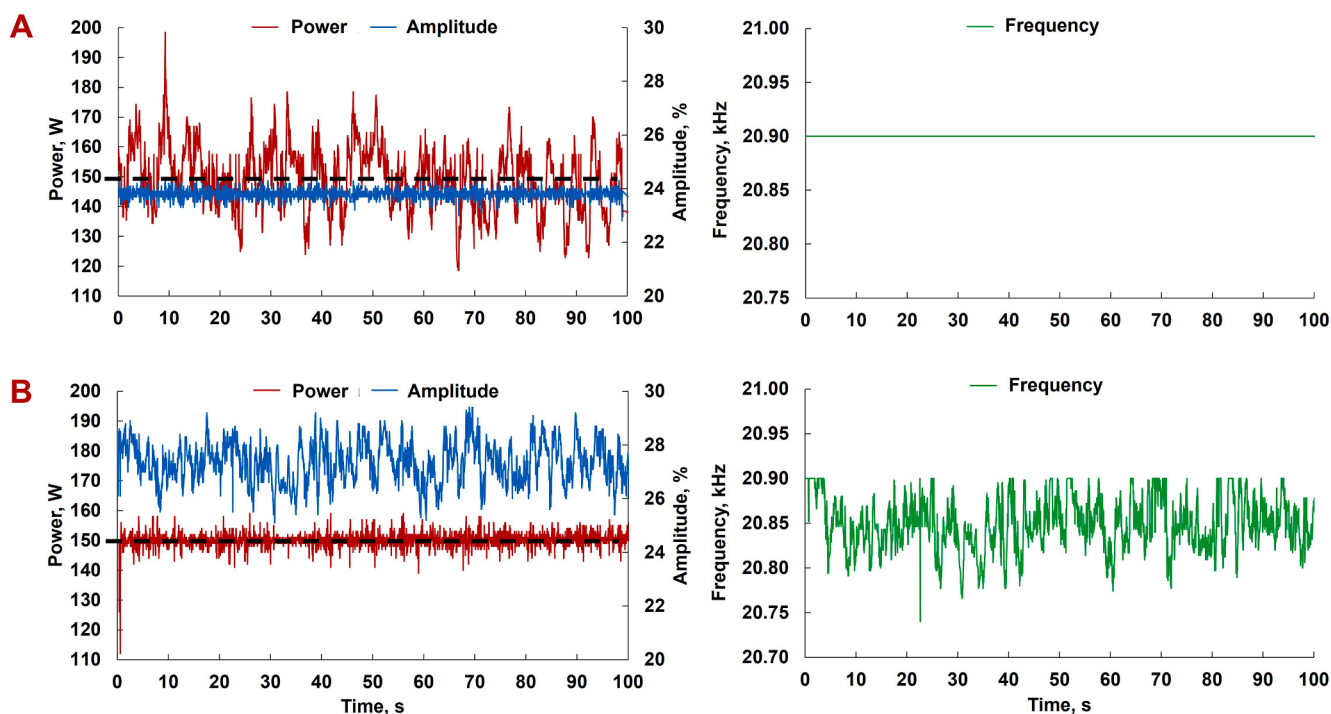


Fig. 2. Power, amplitude, and frequency behavior during the operation controlled by A) amplitude and B) power.

of 600 W, for example, the temperature variation was approximately 10 °C. On the other hand, for 75 W, the inlet and outlet temperatures were virtually the same. In the absence of US, as there was no additional energy source, heat was lost through the walls and temperature consequently decreased as the liquid phase flowed through the system, resulting in higher inlet and lower outlet temperatures.

It is also important to note that, the higher the applied power, the lower the temperature of the liquid phase entering the system should be (*i.e.*, the setpoint of the temperature control unit), so that the average temperature would result in 70 °C. Using a power of 600 W, the energy dissipation was so intense that the desired liquid phase inlet temperature (66.0 °C) could only be obtained by cooling the system by pumping cold water through the temperature control unit. Moreover, as the temperature varied greatly, this condition would not be suitable for a reliable and predictable operation. Therefore, this US power was no longer used throughout the study.

Although the average temperatures for the presented conditions (with and without US) were the same, it is worth noting that the spatial temperature distributions throughout the system were quite different. In the presence of US, mainly for the conditions of greater power, the region close to the discharge section of the system presented a significantly higher temperature than the entry region. In this sense, the comparison of results obtained with and without US would be compromised if these differences were not considered, since different temperature conditions would be applied in each situation. In this sense, to ensure comparable conditions in the presence or absence of US (silent condition), a set of heating collars, which can be seen in Fig. 4, was coupled to the external part of the US applicator to reproduce the temperature profile observed when US energy was used, which will be defined as silent condition. In addition, a heating tape was wrapped around the clamp and waveguide of the US system (not shown) in order to avoid heat loss through these components. Thus, it was ensured that any increase in the extraction efficiency obtained in the presence of US was due to the specific effects of this alternative energy source, originated from the cavitation process, and not from the different temperature distributions throughout the system.

The electrical power consumed by the heating elements was

gradually adjusted, through the use of voltage regulators, until the temperature profile, measured with the aid of a thermocouple, approached that obtained when in the presence of US. The resulting temperature profiles are shown in Fig. 3B. It is possible to observe a great similarity between the temperature profiles, indicating that equivalent conditions of temperature distribution throughout the system were present, permitting a fair comparison between the results obtained. The electrical power consumed by the heating collars to reproduce the temperature profile was  $69 \pm 2$ ,  $124 \pm 4$ , and  $255 \pm 7$  W for the US electrical input power of 75, 150, and 300 W, respectively. It is important to mention that the temperature control unit setpoints were the same as when US energy was used (Fig. 3A).

### 3.3. Ultrasonic power and distribution

The quantification of the power absorbed by the liquid phase was performed by calorimetry [27]. As mentioned before, the US generator controlled the electrical input power of the transducers. Thus, it is well known that losses occur in the conversion of electrical energy to mechanical vibrations, which makes the effective absorbed power lower than the applied one. As temperature profiles were obtained for each condition with and without US, it was possible to calculate the US power absorbed by the liquid phase.

In the condition without US, the liquid phase lost heat through the metallic walls of the system, decreasing its temperature. In this case, the only heat source was the temperature control unit. In this sense, it was possible to estimate the heat loss for this condition, by measuring the temperature at position 0.2 (Fig. 3A), where the liquid phase entered the US applicator, and at 0.9, where it exited the tube. Considering the liquid phase density as  $988 \text{ kg m}^{-3}$  at 70 °C, its flow rate as  $0.37 \text{ L min}^{-1}$ , the heat capacity as  $4,190 \text{ J kg}^{-1} \text{ K}^{-1}$ , and assuming that these parameters remained constant through the length of the system, the heat loss was estimated as 71 W. The same calculation was performed to estimate the absorbed power when US energy was applied. Assuming the heat loss remained the same as previously calculated, since average temperatures along the tube length were virtually the same, the absorbed power was calculated to be 74, 120, and 199 W for the electric input

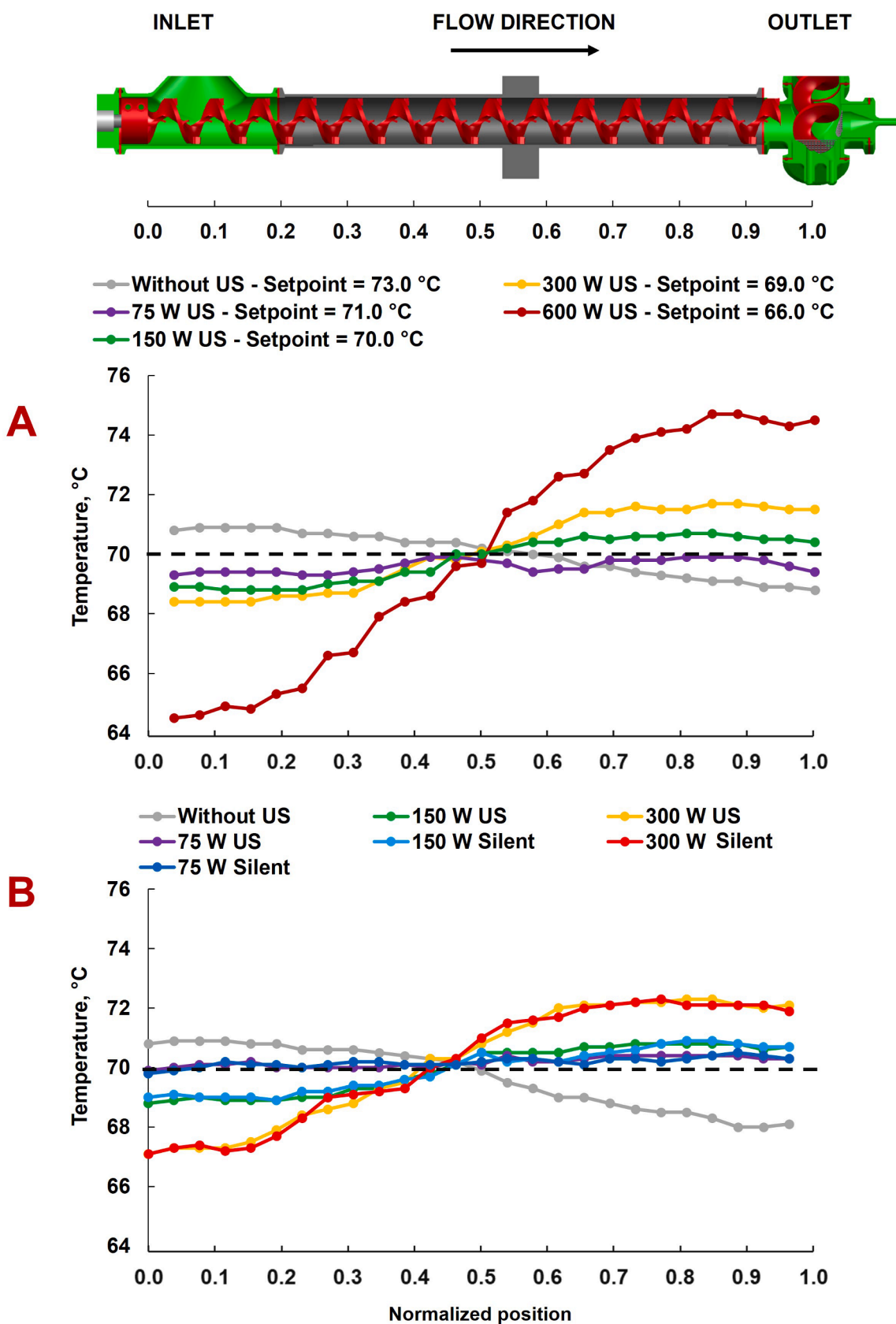


Fig. 3. A) Temperature profiles of the flow extraction system as a function of the evaluated power and B) reproduced temperature profiles obtained with the use of heating collars (silent). Average temperature was 70 °C for all temperature profiles (black dashed lines). The position in x-axis was normalized to the total length of the system (65 cm).

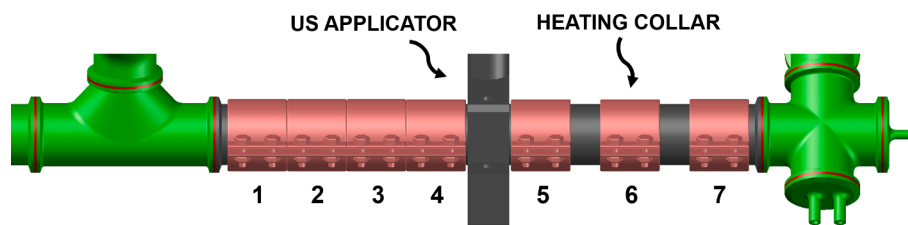


Fig. 4. Heating collars used to reproduce the temperature profile observed when US energy was used for the silent condition.

powers of 75, 150, and 300 W, respectively. Ultrasonic power densities were also calculated for these conditions, being estimated as 71, 114, and 190 W/L, respectively (considering 1.05 L as the internal volume).

The absorbed power was lower than the electrical input power, probably due to the limited conversion efficiency into mechanical oscillations by the transducers [28,29]. Additionally, eventual losses could have occurred during US transmission by the clamp-on tube system. The higher losses observed for the higher electric input powers might be explained by the nonlinear behavior of the US applicator, as well as by the differences in heat loss that were not considered. Moreover, the US applicator might have different conversion efficiencies depending on the electrical input power [28].

An additional experiment was performed to identify the US distribution along the tube length by measuring the acoustic pressure using a hydrophone. The obtained results are shown in Fig. 5.

The obtained pressure distributions show that US energy was relatively well distributed through the system since the whole tube vibrates and transfers to the liquid phase, which is a great advantage of this type of applicator. In this sense, during the extraction process, all the particles inside of the tube would be exposed to US energy, intensifying this process. As expected, the greater the electric input power applied, the greater the resulting acoustic pressure. During the operation of the fully assembled system, the presence of solid particles probably leads to

attenuation and dispersion of sound waves, affecting the values of acoustic pressure presented here. However, they could also act as nuclei for cavity formation, favoring the cavitation process [18].

### 3.4. Dynamic behavior and extraction efficiency

After measuring the temperature distribution and absorbed power, continuous flow extraction experiments were performed. The dynamic behavior of the system, represented by Cr(III) concentration in the extracting solution, in the presence of US and with the use of heating collars to reproduce the temperature profile can be seen in Fig. 6, while Cr(III) concentrations in the treated solid and the respective extraction efficiencies are shown in Fig. 7.

The dynamic behavior of the system was similar for all conditions evaluated during the stabilization time. It is possible to see a rapid increase in Cr(III) in the extracting solution up to  $\theta = 2$  and the steady state was reached when  $\theta \geq 4$ . It is possible to conclude that the dynamic behavior of the system was not affected by US energy since the relative time required for stabilization was not affected.

For  $\tau = 30$  min, it is possible to observe that US increased Cr concentration in the extracting solution from  $210 \pm 5$  (75 W Silent) to  $312 \pm 8$  mg L<sup>-1</sup> (75 W US). No significant increase in efficiency was observed when the electric input power was higher than 75 W (*t*-student test, 95 %

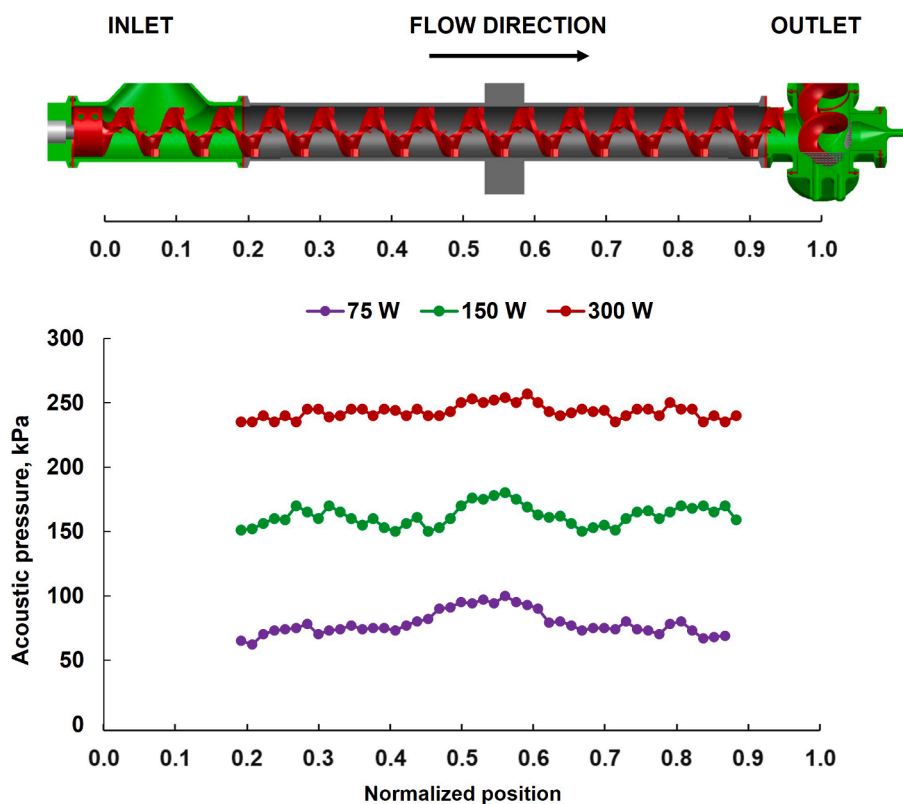


Fig. 5. Acoustic pressure distribution inside of the US applicator for the evaluated electric input powers. The position in x-axis was normalized to the total length of the system (65 cm).

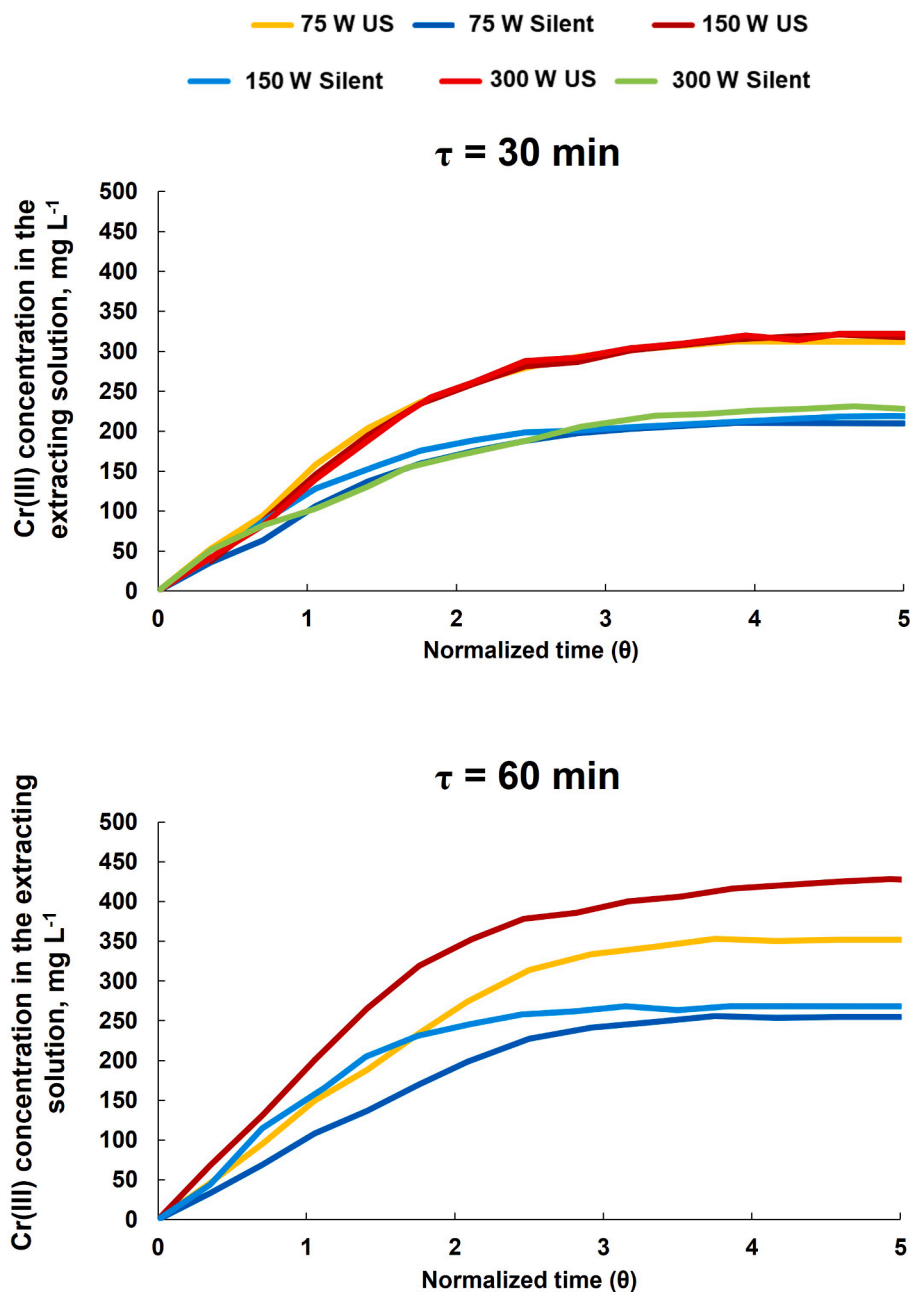


Fig. 6. Dynamic behavior of Cr(III) concentration in the extracting solution in the presence of US and with the use of heating collars to reproduce the temperature profile. Residence times of 30 and 60 min at 70 °C.

confidence level). In this condition, the treated solid presented  $10.5 \pm 0.3 \text{ mg g}^{-1}$  of residual Cr(III), corresponding to an extraction efficiency of  $59.2 \pm 1.1 \%$ .

For  $\tau = 60 \text{ min}$ , Cr(III) concentration increased from  $268 \pm 7$  (150 W Silent) to  $425 \pm 11 \text{ mg L}^{-1}$  (150 W US) in the presence of US. When the power was increased from 75 to 150 W, Cr(III) concentration in the solution increased from  $352 \pm 9$  to  $425 \pm 11 \text{ mg L}^{-1}$ . However, when the 300 W power was evaluated, excessive fragmentation of the solid phase and clogging of the system filters were observed, preventing the correct functioning of the system. Thus, the condition using 150 W US was considered as optimal, with an extraction efficiency of  $71.7 \pm 0.7 \%$  and  $7.3 \pm 0.2 \text{ mg g}^{-1}$  residual Cr(III) content in the treated solid. In this condition, the system was able to operate continuously for more than 12 h without the obstruction of the filters or any other issues.

In the operational conditions with temperatures higher than 70 °C or

residence times over 60 min in the presence of US, the system filters were blocked by a gelatinous and glutinous material, probably due to exposing the protein fraction to a relatively high temperature for a long period in the presence of US. Thus, the effect of US on extraction could be investigated only for temperatures of up to 70 °C and residence times lower than or equal to 60 min.

It is possible to observe that the extraction efficiency obtained for the condition using 150 W US,  $\tau = 60 \text{ min}$  and 70 °C, was higher than that obtained at 80 °C and  $\tau = 60 \text{ min}$  without US ( $71.7 \pm 0.7 \%$  versus  $67.7 \pm 1.0 \%$ , respectively). Therefore, the use of US energy allowed a temperature reduction of 10 °C without losses in extraction efficiency, which is considered as a positive point, since the risk of protein degradation is reduced [7]. Additionally, the US energy could reduce the time necessary to achieve the same extraction efficiency. For example, the efficiency obtained using 75 W of US power with  $\tau = 30 \text{ min}$  ( $59.2 \pm 1.1$



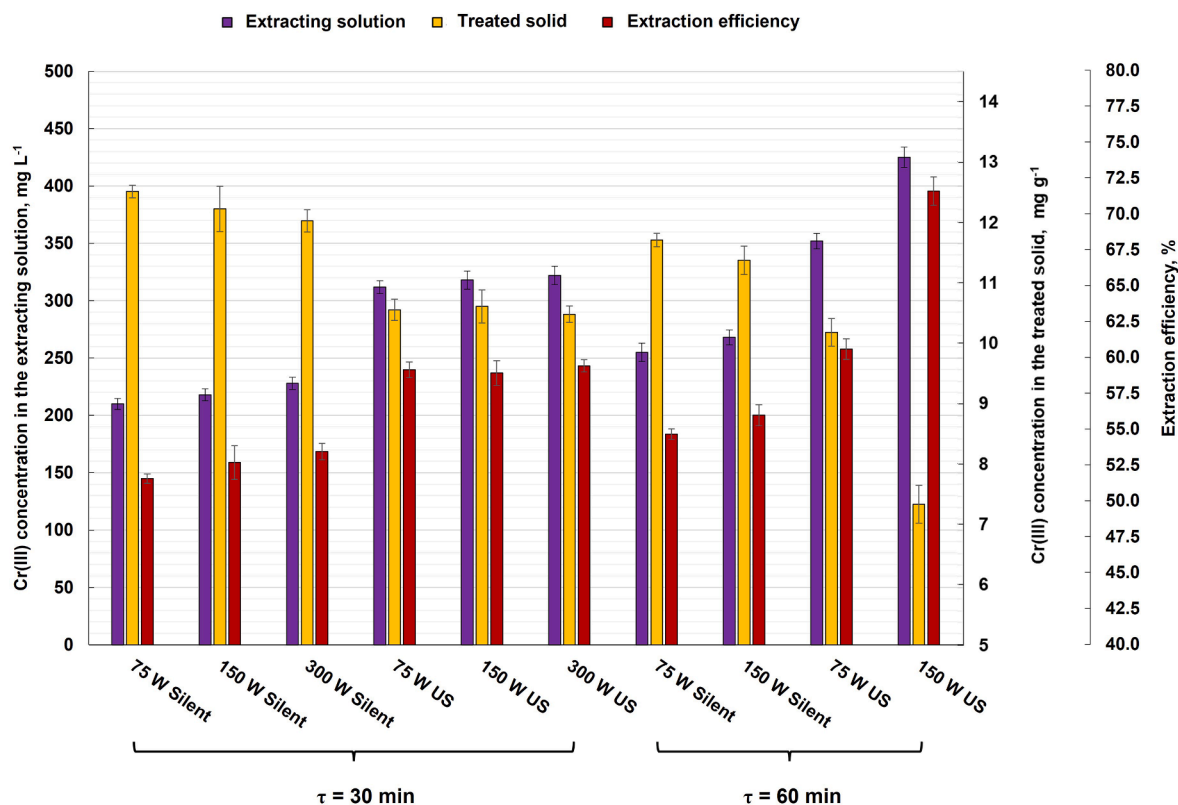


Fig. 7. Chromium(III) concentration in the extracting solution at steady state, in the treated solid, and extraction efficiency in the presence of the US and with the silent condition. Residence times of 30 and 60 min at 70 °C.

%) was higher than the one obtained with  $\tau = 60$  min without US ( $54.7 \pm 0.9$  %, 75 W Silent). Moreover, only after 120 min of extraction without US (75 W Silent, results not presented) an extraction efficiency equivalent to the one obtained with 75 W of US was observed ( $59.5 \pm 1.1$  %). This result shows that US could greatly reduce the time required to reach the same extraction efficiency in the proposed system.

One might notice that when the efficiency obtained for 150 W Silent is compared with the one obtained for 150 W US, an increase of 28.0 % in the extraction efficiency (from  $56.0 \pm 0.9$  to  $71.7 \pm 0.7$  %, respectively) was observed. However, Cr(III) concentration in the treated solid reduced significantly, from  $11.4 \pm 0.3$  mg g<sup>-1</sup> (150 W Silent) to  $7.3 \pm 0.2$  mg g<sup>-1</sup> (150 W US), when US was applied, which corresponds to a reduction of 37.4 %.

Based on these results, it can be concluded that the extraction efficiencies obtained in the presence of US were always higher than those obtained with the silent condition. As the operational conditions were the same in both cases, including the temperature profiles, it is possible to infer that the increase in the process efficiency is due to the specific effects generated by the US. The propagation of the US itself in the liquid and the cavitation process possibly increased the agitation and turbulence of the medium, increasing the mass transfer rates [30]. The implosion of cavitation bubbles in the vicinity of the solid leather particles may have created high shear forces that ruptured structures (as seen by the glutinous aspect of the solid after an excessive exposure time to US) and micro-jets that forced the penetration of the extracting solution through the surface of the particles, intensifying the solute mass transfer rate and, consequently, the extraction yields [30,31]. Additionally, fragmentation of the solid particles could also have occurred as a consequence of the shockwaves created during the collapse of cavitation bubbles, reducing particle size and increasing the surface area, which could consequently increase extraction rates [32]. In addition to the mechanical effects caused by the US, the formation of chemical radicals, due to the breakdown of water molecules and other chemical

species during the implosion of cavitation bubbles, may have affected the chemical stability of Cr(III)-collagen compounds, facilitating the extraction process [7,25]. Moreover, one can understand that the only way to introduce some kind of mechanical agitation to increase mass transfer would be by using the US energy since it is not feasible to perform it in another way without disturbing the system behavior.

When comparing the results obtained for the silent and the condition without US (without heating collars), a relatively small increase in Cr (III) concentration was observed in the extraction solution as the power of the heating collars was increased. This probably occurred due to the higher temperatures obtained in the outlet section of the system, as shown in Fig. 3A. Thus, the solid fraction closer to the outlet section of the system was subjected to higher temperatures than in the condition without US, leading to greater extraction efficiencies. In addition, in the condition without US, the radial temperature gradient was inverted when compared to the condition with the heating collars. Then, the walls of the system were colder than the liquid, since they were exposed to the environment. Consequently, the region of the liquid phase close to the walls had a lower temperature, causing the extraction speed to be reduced at this location, contributing to the relatively lower efficiency observed.

### 3.5. Solid phase chromium concentration profile

The Cr(III) concentration profiles in the solid phase were determined in the presence and absence of US by collecting samples of the solid phase along the length of the screw conveyor for subsequent Cr(III) determination. The obtained results are shown in Fig. 8.

For the condition without US, it is possible to observe a sharp decline in the Cr(III) concentration in the initial part of the system, between the positions 0.0 and 0.3. In the region between 0.6 and 1.0, a less marked decrease in concentration occurred, indicating that the extraction process slowed towards the exit of the system. Possibly, as mentioned

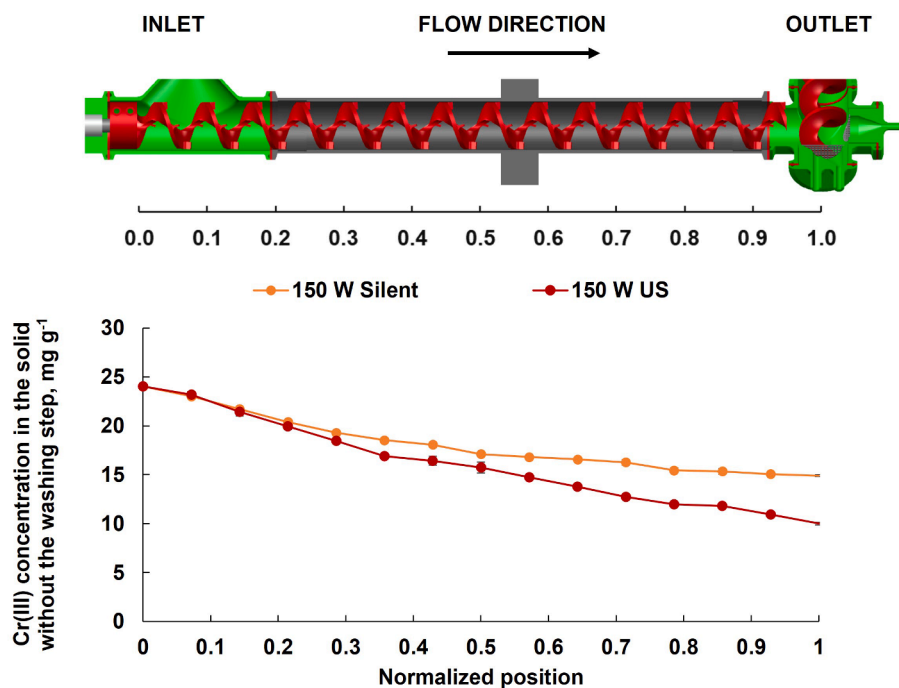


Fig. 8. Solid phase Cr(III) concentration profiles along the system length, for the conditions of 150 W US and 150 W silent. The presented Cr(III) concentration is relative to the solid without washing process. Residence time of 60 min at 70 °C. The position in x-axis was normalized to the total length of the system (65 cm).

before, due to the relatively lower temperature found in this region, added to the decrease in the reaction rate due to the lower concentration of Cr(III) in the solid particles. A similar profile was obtained for the condition of 150 W silent, but the decrease in concentration was more pronounced from the position 0.3 due to the relatively higher

temperature generated by the heating collars, which possibly favored the extraction process. In the presence of 150 W of US, it is possible to see a more intense decline in Cr(III) concentration throughout the whole length of the system, indicating that US intensified the extraction process, corroborating the results presented earlier.

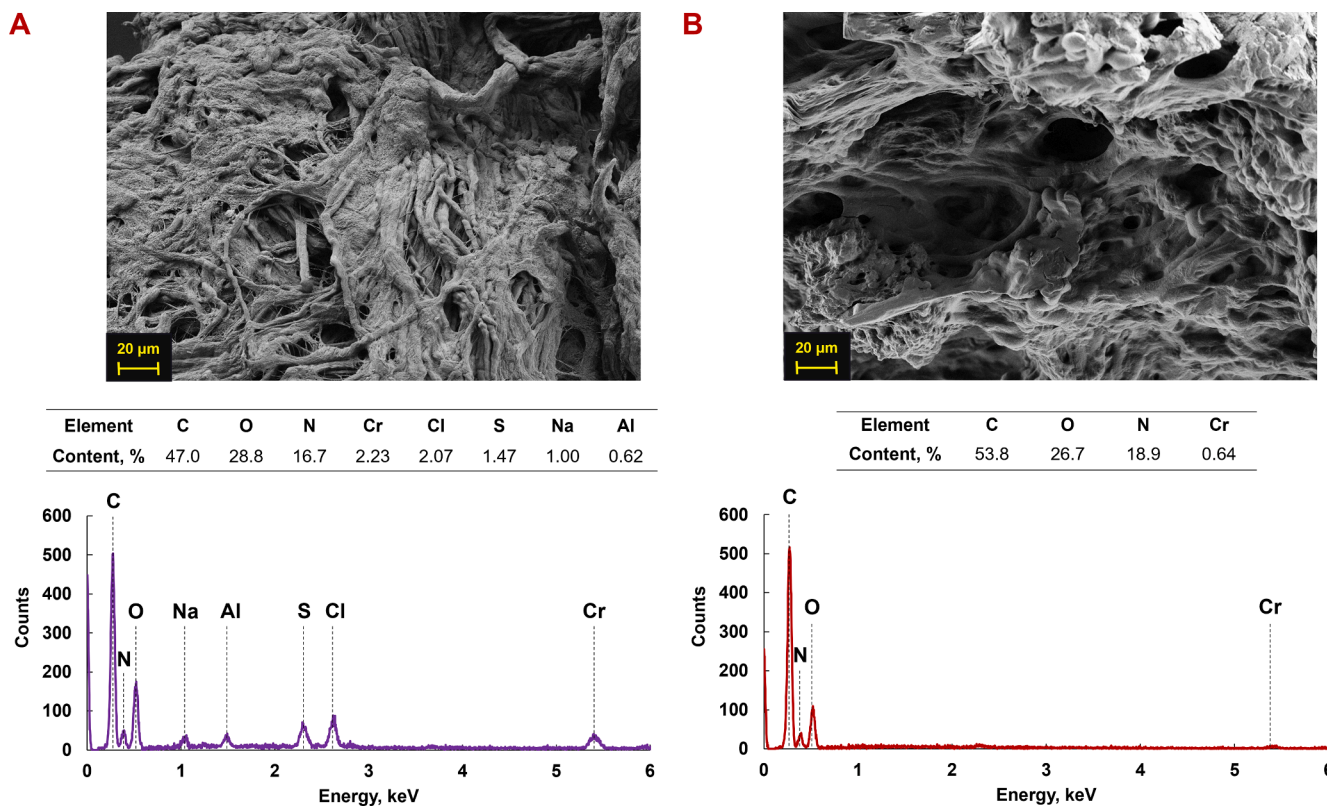


Fig. 9. Visual aspect and spectrum of EDS for the sample of tanned leather A) before and B) after processing in the optimized condition ( $\tau = 60$  min, 70 °C, 150 W US). Magnification of 1000X.

It is noticeable that Cr(III) concentration at the positions of 0.9 and 1.0, at the outlet of the system, still showed a sharp decline in the presence of US. Therefore, if the length of the system were to be increased, an increase in extraction efficiency would also be expected. On the other hand, in the absence of US, the increase in length would not result in significant gains, because a stability profile was observed in the region near the exit of the system.

### 3.6. Solid phase characterization by SEM after extraction

After obtaining the optimized extraction condition, the treated solid was characterized by SEM. The visual aspect of the sample, as well as the EDS spectra, before and after processing, can be seen in Fig. 9.

In the image obtained before processing (Fig. 9A), the fibrillar structure of the collagen of the tanned leather can be observed. The spectrum of EDS indicates the presence of Cr, as well as other constituents of the sample, such as Na, Al, S and Cl. After processing in the optimized condition (Fig. 9B), it can be observed that the fibrillar structure was degraded due to the partial removal of the Cr(III) from the material, which forms cross-links between collagen chains and assists in maintaining the physical structure of the material [2]. A higher porosity can also be observed in the sample, as well as a rougher surface structure, possibly as a result of the mechanical effects generated by the cavitation process, such as microjets [30]. The EDS spectrum shows that much of the Cr(III) has been removed. Additionally, the other constituents of the matrix were also removed (Na, Al, S and Cl), possibly by the action of the extracting solution.

### 3.7. Energy consumption

The electrical power consumed by the system was monitored, with the aid of a wattmeter, during the continuous flow experiments in order to compare the energy consumed in each experimental condition. The obtained results are presented in Table 1. The specific energy consumption was calculated by dividing the energy consumed by the wet solid flow rate.

It is possible to observe that, although a higher extraction efficiency was observed for the 150 W US condition, for  $\tau = 60$  min, in comparison with 150 W silent ( $71.7\% \pm 0.7\%$  versus  $56.0\% \pm 0.9\%$ , respectively), the energy consumption also increase. It occurred because the US

**Table 1**

Energy consumed by the system during the flow extraction experiments for the evaluated conditions. The condition "without US" refers to the one where no heating collars were used.

Condition	Energy consumption, kWh	Specific energy consumption, kWh kg <sup>-1</sup>	Extraction efficiency / Energy consumption, kWh <sup>-1</sup>
$\tau = 30$ min, without US	$1.38 \pm 0.04$	$9.18 \pm 0.24$	5.2
$\tau = 30$ min, 75 W Silent	$1.27 \pm 0.03$	$8.46 \pm 0.22$	6.1
$\tau = 30$ min, 75 W US	$1.41 \pm 0.04$	$9.39 \pm 0.24$	6.3
$\tau = 60$ min, 75 W Silent	$0.986 \pm 0.018$	$13.1 \pm 0.2$	4.2
$\tau = 120$ min, 75 W Silent	$0.918 \pm 0.022$	$24.2 \pm 0.6$	2.5
$\tau = 60$ min, without US	$0.918 \pm 0.025$	$12.2 \pm 0.3$	4.4
$\tau = 60$ min, 150 W Silent	$1.03 \pm 0.02$	$13.6 \pm 0.3$	4.1
$\tau = 60$ min, 150 W US	$1.35 \pm 0.03$	$17.9 \pm 0.3$	4.0
$\tau = 60$ min, without US (80 °C)	$1.31 \pm 0.04$	$17.3 \pm 0.5$	3.9

generator presented a relatively low power factor (about 0.48), due to the presence of reactive power, which increased the total energy consumption [33]. To obtain a similar extraction efficiency, it was necessary to increase the temperature to 80 °C ( $67.7 \pm 1.0\%$ , without US), which resulted in equivalent energy consumption. However, when higher temperatures are used, the risk of protein degradation is higher, which is not desirable [7]. In this sense, the use of US appears to be advantageous, because it allowed operations in a lower temperature while maintaining a high extraction efficiency and consuming an equivalent amount of energy.

As previously discussed, US energy allowed to reduce at least by half the time necessary to achieve the same extraction efficiency. For the operational condition of 75 W US and  $\tau = 30$  min, for example, the total energy consumed was higher than for.

75 W Silent and  $\tau = 60$  min. However, the specific energy consumption, which was calculated by dividing the energy consumed by the solid flow rate, was lower for the condition with US ( $13.1 \pm 0.2$  versus  $9.39 \pm 0.24$  kWh kg<sup>-1</sup>, respectively). Moreover, when comparing to the  $\tau = 120$  min condition, in which a similar extraction efficiency was observed, the specific energy consumption was 2.6 times lower. This result clearly shows that US could reduce the relative amount of energy consumed to achieve the same extraction efficiency. It is important to mention that, for  $\tau = 30$  min, the fresh extracting solution flow rate was double of that used for  $\tau = 60$  min ( $41.8$  versus  $20.8$  mL min<sup>-1</sup>, respectively). Therefore, a higher power was consumed by the temperature control unit to bring the solution to the same temperature.

Another result presented in Table 1 is the extraction efficiency/energy consumption ratio. Higher ratios mean that a high extraction efficiency could be obtained with low energy consumption. Surprisingly, the best ratio was found for  $\tau = 30$  min and 75 W US. For the condition that resulted in the highest extraction efficiency ( $\tau = 60$  min, 150 W US), the ratio was 4.0 kWh<sup>-1</sup>, whilst a similar ratio was observed for the respective silent condition (4.1,  $\tau = 60$  min, 150 W Silent). It occurred because both extraction efficiency and energy consumption were reduced in the same proportion for this last condition. The increase in extraction efficiency observed when comparing 30 and 60 min of residence time was not high enough to compensate for the increased energy consumption of the longer residence time, being the reason why the extraction efficiency/energy consumption ratio was lower for these conditions.

The power factor for the condition using 75 W US was about 0.42, as well as for 150 W US (0.48), which can be considered low. Probably, it occurred because the US generator was operating only with a fraction of the maximum rated power (1000 W), which may have led to relatively low energy efficiency. If necessary, the power factor could be corrected by using tailored designed inductors or capacitors coupled to the electrical input of the US generator, bringing the power factor closer to 1.0 and reducing energy consumption [34]. Additionally, after defining the optimum operating power, a correctly sized US system could be developed for the application, which would probably lead to better energy efficiency. As the system used in this work consisted of an experimental prototype, which underwent several modifications and reconfigurations throughout the work, no efforts were made to improve the thermal efficiency of the system. In this sense, it is believed that by improving the thermal insulation of the system, the heat dissipation to the environment would be reduced and, consequently, the energy consumption.

## 4. Conclusions

In this work, the feasibility of using US to intensify the continuous flow Cr(III) extraction from tanned leather shavings using a 3D printed system combined with a tubular US applicator was demonstrated. The US energy allowed a reduction in processing time and operational temperature when compared to the silent condition. The overall energy consumption with US was similar or lower than that observed without US, showing the feasibility of this alternative energy.

Finally, although  $71.7\% \pm 0.7\%$  of the initial Cr(III) was removed, the residual Cr(III) concentration was still relatively high, possibly preventing the direct use of the treated solid. In this way, future work should aim to somehow increase the extraction efficiency, for example, by increasing the system length or by modifying the design to allow the operation with smaller solid particles. Moreover, the system printing files can be shared with anyone who wants to reproduce the system and use it for other applications.

### CRedit authorship contribution statement

**Matheus F. Pedrotti:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft. **Daniel Santos:** Formal analysis, Investigation. **Vitoria H. Cauduro:** Formal analysis, Investigation. **Cezar A. Bizzi:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Erico M.M. Flores:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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