

Article

Combination of Thermal, Hydrometallurgical and Electrochemical Tannery Waste Treatment for Cr(III) Recovery

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Abstract: A combination of thermal (500–750 °C in air) and hydrometallurgical (acidic) treatments have been applied to dried tannery sludge, resulting in the initial conversion of Cr(III) to Cr(VI) and its subsequent leaching as wastewater with high Cr(VI) concentration content (3000–6000 mg/L), presenting an extraction efficiency over 90%. The optimal electrochemical conditions for the subsequent Cr(VI) reduction with respect to acid concentration and acid kind were established by applying appropriate rotating disc electrode (RDE) experiments, using a glassy carbon (GC) electrode, and found to be equal or higher than 0.5 M H₂SO₄ (for the respective Cr(III) concentration range studied). The result from leaching Cr(VI) wastewater was further treated in small electrochemical bench-scale reactor for its conversion back to Cr(III) form, potentially reusable in the tanning industry. Ti-based anodes and a reticulated vitreous carbon (RVC) cathode were used to treat small (350–800 mL) samples in batch, as well as in batch-recirculation prototype electrochemical reactors, under the application of constant current or appropriately applied potential to achieve Cr(VI) conversion/reduction efficiency over 95%.

Keywords: chromium recovery; tannery waste; hydrometallurgy; electrochemistry; Cr(VI) reduction



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1. Introduction

Tanneries can transform raw skin into leather, by using physico-chemical and mechanical techniques. The main chemical reagents, used to produce leather with desired commercial properties, are based on Cr(III) salts. However, due to the low effectiveness of the aforementioned tanning processes, tanneries produce large quantities of hazardous wastewaters [1]. In order to treat this waste, several physico-chemical and biological methods can be applied, resulting in sludge production with high chromium and organic matter content. Aiming at the minimization of environmental impact, the disposal options of tannery sludge has to be considered carefully (hazardous limit is 70 mg Cr_{total}/Kg), and more sustainable management options should be promoted [2].

Following the suggestions of international environmental organizations, many researchers have studied and proposed alternative methods for the environmental sound management of tannery sludge. A specific case, generating great interest and showing certain prospects, is the application of thermal treatment, whether it concerns energy recovery [3], or as an intermediate stage of a more complex process [4]. The main feature that makes thermal treatment attractive is the great reduction in sludge volume, due to the combustion of organic matter content [5].

However, the application of increased temperatures can cause the oxidation of trivalent chromium to its highly toxic, carcinogenic and mutagenic hexavalent form (LD₅₀ = 50–150 mg/Kg) [6]. Simultaneously, Cr leaching can be achieved under milder

conditions, due to the much higher solubility of hexavalent chromium. While the Cr(VI) oxyanions are very mobile (and toxic), Cr(III) cations are much less so and, instead, they can form the insoluble precipitate Cr(OH)₃, which is easily separated [7]. Therefore, by reducing Cr(VI) to Cr(III) the final removal (and recovery for reuse in the tanning process) of chromium from the effluent/leachate can be achieved easily by precipitation [8,9].

Several methods have been reported for the reduction of hexavalent chromium to its trivalent form in industrial wastewaters, including some originating from tanneries [10]. Chemical reduction by using SO₂, NaHSO₃ and FeSO₄ as reducing agents [11,12] is a typical treatment method, which is not very satisfactory, because of the respective use of chemicals, possibly creating secondary pollution problems and large amounts of produced sludge. Biological methods, involving e.g., bacteria [13] or fungi [14], for the reduction of Cr(VI) to Cr(III) are alternatives to conventional methods; however, their efficiency is sometimes limited, since the toxic metals (including Cr) can attack and destroy the membranes and the tissues of the used microbes.

The drawbacks of the previously mentioned methods can be avoided by the application of electrochemical treatment, which appears to be greener and more effective in comparison with traditional technologies. They can be applied either indirectly, such as electro-coagulation [15], which involves the dissolution of a sacrificial anode made usually of iron or aluminum [16], or directly, such as electro-reduction, in which the free electrons, supplied by a power source through an appropriate electrode, can act as the reducing agent. When the techniques of chemical reduction, electrochemical reduction (with electro-generated Fe(II)) and direct electro-reduction of Cr(VI) have been compared [17], it was found that the consumption of energy was higher for the case of electro-reduction. Despite this fact, direct electro-reduction has turned out to be the cleanest method, because it does not result in the contamination of sludge with iron.

In the electro-reduction technique, the cathode material is very important. Carbon-based materials such as graphite felt, fibrous carbon and reticulated vitreous carbon (RVC) [18–20] have successfully been used. Stainless steel and titanium electrodes [17,21] have also been reported. RVC has been selected in most studies as the cathode material, mainly because of its higher surface area and its porous structure that creates local turbulence, improving mass transfer [22]. Although the passivation of the RVC electrode in contact with chromate ions has been reported [23], it was found elsewhere that the direct Cr(VI) reduction in both synthetic and field samples can be practically 100%, by using the RVC cathode in a parallel-plate flow-by reactor and applying a relatively low voltage value [20].

Most of the aforementioned electrochemical treatment studies deal with effluents, containing relatively small amounts of Cr(VI) (typically less than 1000 mg/L) and aim to reduce its levels below 0.5 mg/L [20], so that it can be safely discharged, according to environmental regulations. A typical application, similar to the previous conditions, is the treatment of rinse wastewaters, originating from the Cr plating industry. As far as we know, we are not aware of any study, dealing with the treatment of concentrated Cr(VI) solutions, such as those originating from chromium leaching from thermally treated tannery sludge by acid extraction, aiming at electrochemical Cr(III) regeneration and potential reuse in tanneries.

The aim of this study is to optimize and maximize the recovery of chromium from tannery sludge by a sequence of thermal, hydrometallurgical and electrochemical treatment techniques. The specific objectives have been the following: (a) the establishment of appropriate thermal treatment conditions for the quantitative oxidation of Cr(III) to Cr(VI) in the resulting solid waste; (b) the establishment of appropriate acid extraction conditions (acid kind and concentration) for the quantitative Cr(VI) leaching from the solid waste; and (c) the optimization of main experimental conditions (i.e., acid concentration, electrodes, operation of reactor) for the quantitative regeneration of Cr(III) by the application of direct electrochemical reduction of Cr(VI), using RVC electrodes in prototype batch and batch-recirculation type reactors.

2. Materials and Methods

2.1. Sample Preparation

Reference samples were obtained from tannery air-dried sludge of the central wastewater treatment plant, serving the tannery enterprises cluster and based in the main industrial area of Thessaloniki (Sindos—Northern Greece). Prior to thermal treatment, the initial sludge was ground and sieved (<0.5 mm) in order to be homogenized. Afterwards, it was incinerated at the temperature range of 500–750 °C for 2 h, in an electric furnace (model Wisd Muffle Furnaces, manufacturer Witeg, Wertheim, Germany), under the presence of air.

2.2. Characterization

The main structural phases of samples were identified by X-ray diffractometry (XRD), using a water-cooled Rigaku Ultima diffractometer with CuK α radiation, a step size of 0.05° and a step time of 3 s, operating at 40 kV and 30 mA. The diffraction patterns compared to the respective powder diffraction files (PDF) database [24].

Chemical analysis of the samples was conducted by the application of acid digestion, as optimized for the specific samples. Typically, 0.5 g of sample powder was placed in a 100 mL PTFE beaker with 20 mL of concentrated HNO $_3$ and refluxed on a heated plate at 95 °C for 24 h. In contrast to the common leaching procedure, this step does not apply, when the concentrated HCl is used as leaching agent, as in that case a significant portion of hexavalent chromium would be expected to reduce to its trivalent form. Major metal components (Cr, Ca, Mg etc.) were determined by flame atomic absorption spectrophotometry, using a Perkin-Elmer AAnalyst 800 instrument [25], and Cr(VI) was measured by the standard 1,5-diphenylcarbazide colorimetric method, using a Hitachi U-2000 spectrophotometer at 540 nm [26]. Other parameters, such as pH and electrical conductivity, were determined by leaching with deionized water, at a liquid-to-solid ratio (L/S) equal to 25. The organic carbon content measured by the TOC-VCSH E200V Shimadzu Total Organic Carbon (TOC) analyzer and the inorganic carbon by the BD Inventions (model FOG L) calcimeter [27].

2.3. Hydrometallurgical Experiments

The leaching of chromium from the thermally treated samples was conducted according to the common hydrometallurgical protocols by examining various acidic agents. A given quantity of the solid was placed in a beaker and the leaching medium was added. The acids examined were HCl, HNO $_3$ and H $_2$ SO $_4$, in the concentration range 0.05–2 N. The rest of the experimental conditions remained constant, i.e., contact time 60 min, temperature 25 °C and liquid-to-solid ratio (L/S) equal to 25. After the extraction stage, the liquid phase separated by membrane filtration under vacuum and the major metal component concentrations (namely Cr and Ca) were determined in the filtrate.

2.4. Electrochemical Experiments

Preliminary electrochemical experiments, aiming to establish the appropriate acid kind and concentration for the Cr(VI) electrochemical reduction, were carried out by using a 3 mm diameter glassy carbon (GC) rotating disc electrode (RDE, Metrohm), in a three compartment small electrochemical cell (200 mL), equipped with a KCl-saturated calomel reference electrode (SCE) and a Pt-foil counter electrode. All three electrodes were placed in different compartments, separated by a lugin capillary (reference electrode) and a glass frit (counter electrode). Linear sweep voltammetry experiments (i.e., current recording when the applied potential has been varied at 10 mV·s $^{-1}$ sweep rate) were carried out with the help of an Autolab PGSTAT302N (Eco Chemie) workstation and controlled via the NOVA 1.11.2 software.

For the electrochemical treatment of Cr(VI) leachates both batch and batch-recirculation prototype reactors were used and constant current or voltage in the two-electrode setup was supplied by a DSC—ELECTRONICS, model DP60-15H, 60 V–15 A power supply.

The batch reactor consisted of a cylindrical vessel (400 mL capacity), a 4 cm × 3.3 cm × 0.4 cm RVC cathode (60 ppi, Goodfellow Ltd.) and a 7.5 cm × 3.5 cm × 0.5 cm platinized Ti anode. The latter was prepared by a variation of galvanic replacement technique presented in [28], using a 5×10^{-4} M K_2PtCl_6 + 0.1 M $HClO_4$ solution (prepared from potassium hexachloroplatinate 99% trace metals basis, Aldrich and perchloric acid 70%, Merck). Thorough mixing was achieved via constant magnetic stirring.

For the electrochemical treatment of 800 mL of Cr(VI) leachate placed in a glass container, an original parallel plate-and-frame flow cell was constructed from polypropylene. The plates and the frame had a cross-sectional area of 300 cm² (20 cm × 15 cm); the frame was 1.5 cm thick and its void had a hexagonal shape of a cross-sectional area of 155 cm², resulting in a solution capacity of 232.5 mL. The gaskets were made from PTFE (i.e., Polytetrafluoroethylene), which provided good sealing and chemical resistance. The two end-plates carry two circular stainless steel current collectors (5 cm diameter) and the entrance and exit ports for the solution (2 cm diameter). The stainless steel current collectors connected to the outside of cell by stainless steel threaded bars screwed into the cell. The anode was 5 × 2.5 cm plate of a Metcote ES2 IrO_2 anode (ICI) and the cathode an RVC foam (61 ppi, Goodfellow Ltd.). Both electrodes were attached to the current collectors by using carbon cement (WPI, Inc.). A peristaltic pump was employed to achieve a 33 L h⁻¹ volumetric flow rate (Figure 1).

Samples were taken at 30 min (for the small batch reactor experiments) or at 2 h intervals (for the batch-recirculation reactor configuration) and the Cr(VI) concentration was measured by the standard 1,5-diphenylcarbazide colorimetric method (see also the previous Section 2.2).

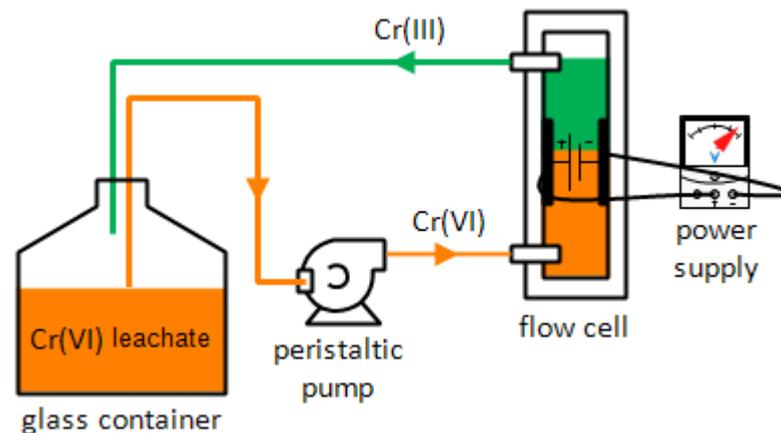


Figure 1. Flow diagram of the batch-recirculation prototype reactor experimental set-up.

3. Results

3.1. Subsection Samples Characterization

According to the X-ray diffraction (XRD) spectra (Figure 2), in all thermally treated samples, the peaks related to the presence of chromium were attributed to the hexavalent form $CaCrO_4$ (Joint Center for Powder Diffraction Studies—JCPDS card No. 08-0458), except for the samples treated at 750 °C, where the observed peaks were attributed to the trivalent form $MgCr_2O_4$ (JCPDS card No. 10-0351). It should be clarified that the identification of chromium's form in the initial tannery sludge was not possible, due to the amorphous structure of these samples. Instead, the crystallinity increased after the thermal treatment, resulting in the appearance of sharp peaks. The remaining peaks of these spectra present mainly the $CaCO_3$ -calcite (JCPDS card No. 47-1743) and the anhydrous $CaSO_4$ (JCPDS card No. 37-1496). The intensity of calcite peaks decreased as the treatment temperature increased, due to its decomposition, while in the case of anhydrite $CaSO_4$, they remain almost unaffected in the examined temperature range.

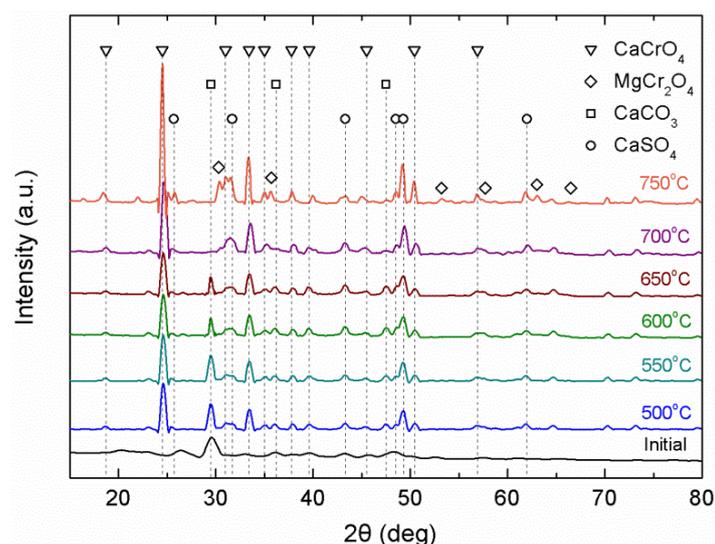


Figure 2. X-ray diffraction (XRD) diagrams of raw tannery sludge and the corresponding ashes after the application of thermal treatment.

As Table 1 shows, a significant weight loss was observed, slightly higher than 50% and almost stable, for all the examined treatment temperatures. These results can be attributed to dehydration/dehydroxylation processes, organic carbon combustion and calcium carbonate decomposition, which mainly took place at temperatures below 500 °C. Such a weight loss led to almost doubling of metal content in the corresponding residues/ashes. Also, it was verified that the initial tannery sludge contained only Cr(III), whereas after the application of thermal treatment, the dominant species were Cr(VI), results which are in good agreement with the respective XRD spectra. The importance of pH and electrical conductivity measurements lies in the determination of appropriate equilibrium conditions during the following hydrometallurgical process, i.e., the dominant species of eluted/leached ions and their corresponding quantity, respectively. In fact, all samples (i.e., the primary waste and the resulting ashes) have been shown to be highly alkaline materials, due to the dissolution of calcium compounds. In contrast, the quantity of leached ions after combustion was substantially higher than that in the initial sludge, according also to the corresponding electrical conductivity measurements. These results can be attributed to the decomposition of organic matter, leading to the production of soluble ash constituents and, therefore, the release of more dissolved ions.

Table 1. Physico-chemical characterization of raw tannery sludge and the corresponding ashes after the application of thermal treatment.

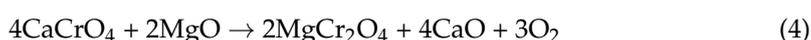
	Treatment Temperature (°C)						
	Initial	500	550	600	650	700	750
	% w/w						
Weight loss	-	52.6	52.8	53	54.5	55.4	55.5
Organic matter	22	1.4	0.2	0	0	0	0
Organic carbon	12.2	0.8	0.1	0	0	0	0
Inorganic carbon	3.1	1.7	1.3	0.8	0.4	0.1	0.1
Cr _{total} :	14.1	28.3	28.5	28.5	28.6	29	29
-Cr(III)	14.1	6	5.7	4.5	3.5	3	3.2
-Cr(VI)	-	22.3	22.8	24	25.1	26	25.8

Table 1. Cont.

	Treatment Temperature (°C)						
	Initial	500	550	600	650	700	750
	% w/w						
Ca	14.8	28.8	29.1	29.3	29.7	29.8	30
Mg	2.4	4.9	5	5.1	5.1	5.1	5.1
Na	1.5	3	3	3.1	3.2	3.2	3.2
Al	0.5	1.1	1.1	1.2	1.2	1.2	1.2
Fe	0.46	0.5	0.5	0.5	0.5	0.6	0.6
K	0.12	0.25	0.25	0.26	0.26	0.27	0.27
Zn	0.06	0.14	0.14	0.14	0.15	0.16	0.16
pH	9.1	9.2	9.2	9.2	9.2	9.2	9.2
Conductivity (mS/cm)	0.96	7.35	7.38	7.4	7.43	7.44	7.43

3.2. Cr(III) Oxidation by Thermal Treatment

Regarding the oxidation mechanism of Cr(III), heat treatment under aerobic conditions is necessary, as in the case of pyrolysis (i.e., under anaerobic conditions) this will not take place [5]. Initially, the dominant form of Cr(III) in the raw sludge is considered to be Cr(OH)₃, since this was precipitated from the wastewater during its primary treatment. However, through the dewatering process in the temperature range 150–250 °C, the requirements for the oxidation of Cr₂O₃ were fulfilled [6], according to Reaction (1). Cr(III) is oxidized in the presence of atmospheric oxygen, while the application of thermal/heating treatment increased both the reaction rate and efficiency [29].



Furthermore, the presence of other metal oxides enhances the oxidation reaction [30]. As the chemical characterization of the sample has proven, the tannery sludge contained high amounts of calcium [31]. However, the dominant form in the sludge is CaCO₃ and thus, in order for Reaction (3) to proceed, a prior step is required, namely Reaction (2). The decomposition of CaCO₃ was essential and became possible in the temperature range examined [4]. The combination of Reactions (2) and (3) is considered to be the dominant oxidation mechanism, since the Cr(VI) is present in the thermally treated samples as CaCrO₄, according to XRD spectra. In addition, the CaCO₃ content in the corresponding ashes was inversely proportional to the determined Cr(VI) percentage up to 700 °C (Figure 3). A further increase in treatment temperature (e.g., over 750 °C) led to a partial reduction of Cr(VI) to Cr(II), since the more stable compound of MgCr₂O₄ was formed, due to the presence of MgO, according to Reaction (4) [32].

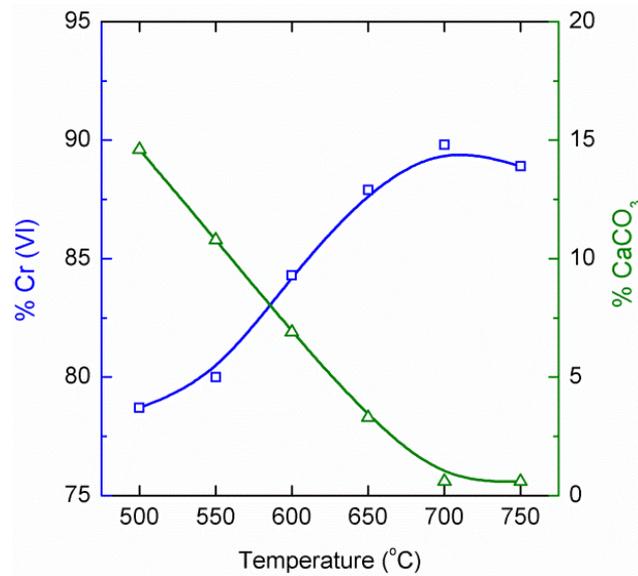


Figure 3. Correlation of Cr(VI) content with the percentage of the CaCO₃ content.

3.3. Hydrometallurgical Extraction of Cr

The recovery of chromium from tannery sludge ash was examined in the sample that presented the highest percentage in the metal's hexavalent form content, namely thermally treated at 700 °C. As approximately 90% of total chromium content (Cr_{total}) existed in the Cr(VI) form, a high extraction rate was also expected. Indeed, according to Figure 4, over 90% of the Cr_{total} was leached, when 1 N of the examined acids was applied. The further increase in acid concentration presented no significant improvement in the leaching efficiency. Moreover, the L/S ratio equal to 25 proved to be suitable for extracting the majority of the initial Cr_{total} under the aforementioned experimental conditions, a value that directly correlated with the metal's content in the raw tannery sludge [7].

In addition, regarding the mechanism of extraction, the application of various acids causes rather insignificant differences regarding efficiency and, also, considering the standard deviation bars. This is attributed to the extremely soluble Cr(VI) species, which is the dominant form of chromium in the resulting ash. Accordingly, due to the presence of the almost insoluble Cr(III) form, a relative stability in the leachable Cr_{total} was observed for the highly acid normality values. Furthermore, the limited extraction at acids' concentration below 0.25 N was observed, due to its partial consumption of acid for the preliminary neutralization of alkaline ions [6]. The presence of such ions was indicated by the pH and electrical conductivity measurements.

By contrast, the leaching by acids presented notable variations, regarding Ca extraction (Figure 4). Considering the selectivity of this process, its leachability of Ca was also investigated, since it was proved from the chemical characterization of the samples that the tannery sludge ashes contained high levels of Ca, equal to those of Cr. When H₂SO₄ was employed, Ca formed the insoluble in acidic media CaSO₄ compound and therefore, less Ca was transferred to the leaching solution [33]. Moreover, the CaSO₄ formation was proportional to acid normality and, thus, for concentrations above 1 N Ca extraction was minimized. Instead, both HNO₃ and HCl proved capable to extract most of the Ca content, while the difference between them was attributed to the slightly higher solubility of the respective metal nitrate salt [34].

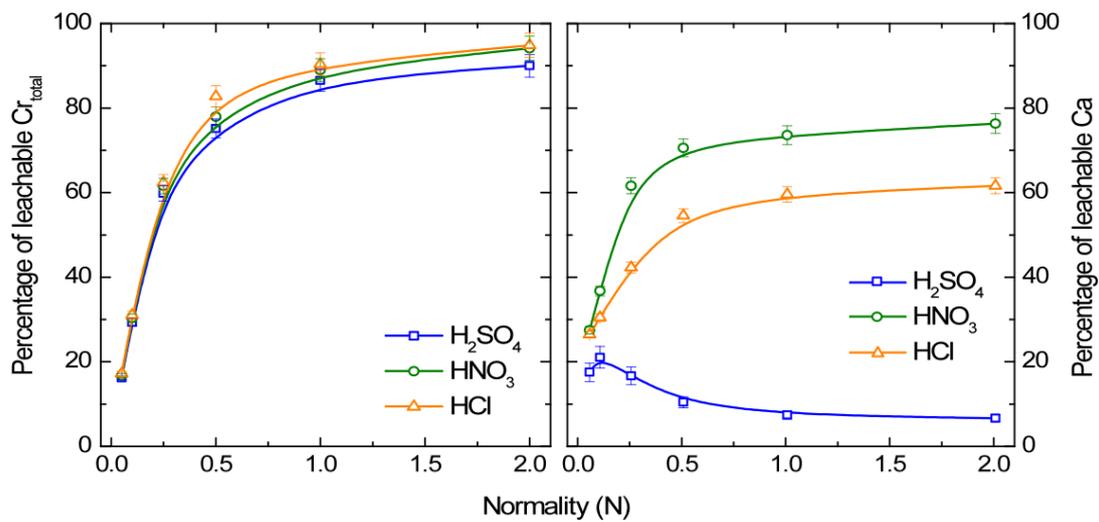


Figure 4. Cr_{total} and Ca extraction from the thermally treated tannery sludge at 700 °C, using different common acids, applied in different (initial) concentrations.

3.4. Electrochemical Reduction of Cr(VI)

3.4.1. Exploratory Voltammetry Using a Glassy Carbon Rotating Disc Electrode

Figure 5 presents the linear sweep voltamograms (LSVs; current vs. potential curves recorded as the potential is varied at a 10 mV·s⁻¹ potential scan rate), obtained with the use of a GC RDE (at a 200 rpm rotation speed) in a solution containing 0.05 M K₂Cr₂O₇ in the presence of either 0.5 M HCl or 0.25 M H₂SO₄. Since Cr(VI) at pH < 1 is known to exist mainly in its HCrO₄⁻ form [35], the negative currents correspond to the following electrochemical Reaction (5) [36].

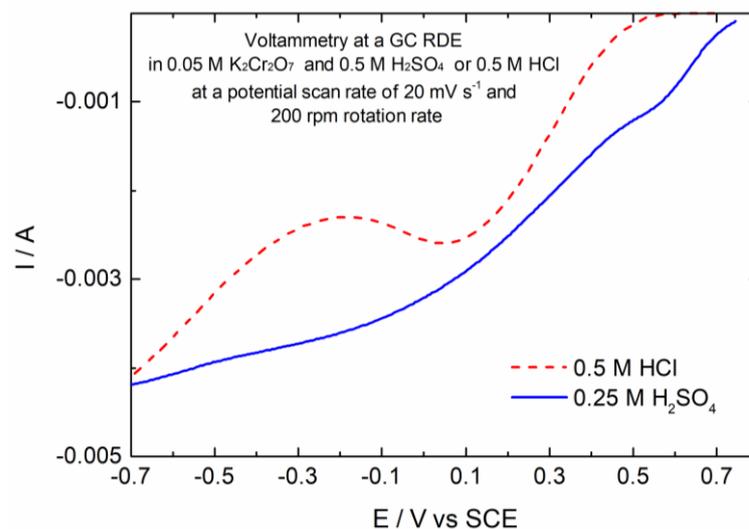
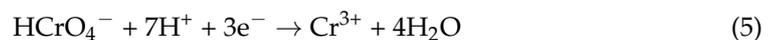


Figure 5. Current vs. potential linear sweep voltamogram (LSV) curves, recorded with the use of a glassy carbon (GC) rotating disc electrode (RDE) at a 200 rpm rotation speed and a 20 mV·s⁻¹ potential scan rate, in 0.05 M K₂Cr₂O₇ solutions, containing 0.5 M HCl or 0.25 M H₂SO₄.

Both LSV curves coincide at similar currents of ca. 4 mA at the most negative potential applied (-0.70 V vs. SCE), where electrode kinetics are expected to be fast and the current controlled by mass transfer. However, they differ significantly in terms of their current onset potential and shape (at the lower negative potentials in the mixed/kinetic control regime). In the presence of Cl^- ions, the onset potential is more negative and there is also a significant current decrease at ca. -0.20 V vs. SCE. Note also that a similar difference between HCl and H_2SO_4 has been reported for the Cr(VI) reduction by using an Au electrode [37]. The adverse effect of HCl acid on HCrO_4^- reduction may be due to the stronger Cl^- anion adsorption on carbon [38] (i.e., competitive to HCrO_4^- adsorption), as well as to the low solubility of CrCl_3 , which may precipitate on the electrode surface, produced after the Cr(III) reaction with Cl^- ions.

Having established that H_2SO_4 is the best selection for the electrochemical treatment of Cr(VI) solutions, the optimal acid concentration should be subsequently identified. Figure 6 presents the LSV curves obtained with the GC RDE (at 1600 rpm) in 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ solutions of different sulfuric acid concentrations in the 0.05–1 M range. For acid concentrations below 0.5 M H_2SO_4 (i.e., with 1 M of protons available for reaction), there is a strong effect of acidity on the Cr(III) reduction currents. This is to be expected since, according to Reaction (5), seven protons take part in the electro-reduction of one Cr-containing specie; hence 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ require a minimum of $2 \times 0.05 \times 7 = 0.7$ M of protons.

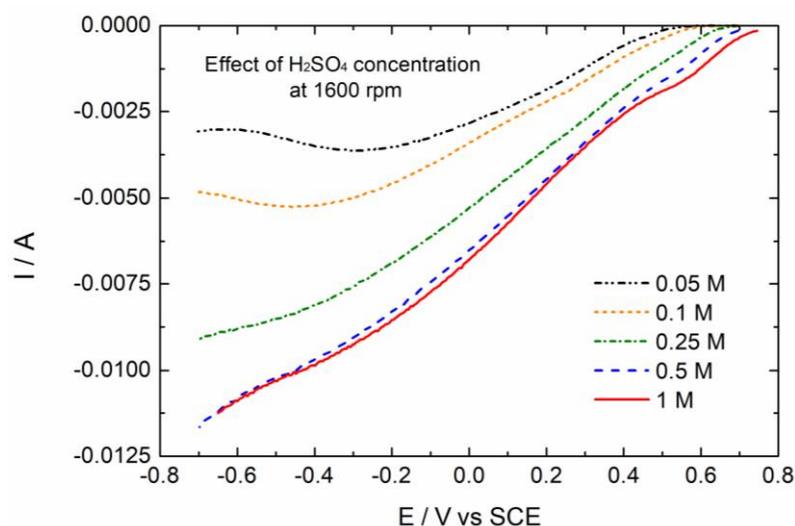


Figure 6. Current vs. potential LSV curves, recorded with a GC RDE electrode at 1600 rpm rotation speed and $20 \text{ mV} \cdot \text{s}^{-1}$ potential scan rate, in 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ solutions of varied H_2SO_4 concentrations.

Finally, Figure 7 presents the effect of rotation rate (mass transfer) conditions in 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7 + 0.5$ M H_2SO_4 solution at rotation rates (f) in the 200–2500 rpm range. It can be observed that the current at potentials more negative than ca. 0.60 V increases with the rotation speed, indicating mass transfer control (partial or complete); by contrast, the ill-defined wave at the foot of the curve (in the ca. 0.70–0.60 V range) remains largely unaffected, further confirming that it corresponds to a HCrO_4^- adsorption pre-wave. Considering, also, the area $A = 0.07065 \text{ cm}^2$, maximum reduction currents are in the 70–190 $\text{mA} \cdot \text{cm}^{-2}$ range.

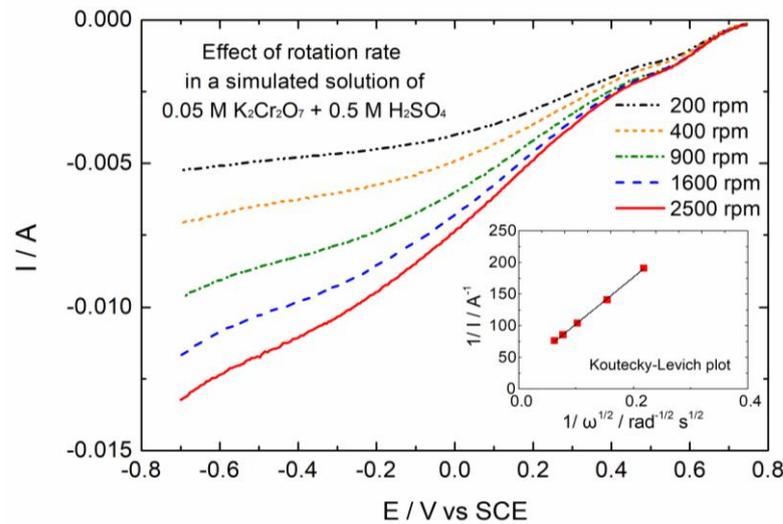


Figure 7. Current vs. potential LSV curves, recorded with GC RDE electrode at various rotation speeds (in the 200–2500 rpm range) and a $20 \text{ mV} \cdot \text{s}^{-1}$ potential scan rate, in a $0.05 \text{ M K}_2\text{Cr}_2\text{O}_7 + 0.5 \text{ M H}_2\text{SO}_4$ solution. Inset: Koutecky–Levich plot for currents at -0.6 V vs. KCl-saturated calomel reference electrode (SCE).

The Inset shows the corresponding Koutecky–Levich plot [39] (i.e., $1/I$ vs. $1/\omega^{1/2}$, where $\omega = 2\pi f$ the rotational velocity in rads^{-1}) for the currents recorded at -0.6 V vs. SCE.

$$\frac{1}{I} = \frac{1}{I_{\text{kin}}} + \frac{1}{0.62nFACD^{2/3}\omega^{1/2}\nu^{-1/6}} \quad (6)$$

Equation (6) gives the reciprocal of the total current measured as the sum of two contributions, i.e., a kinetic (the first term, I_{kin}) and a mass transport (the second term). From the slope of the inset of Figure 6, assuming the number of electrons $n = 3$ (according to Reaction (5)), and taking $F = 96453 \text{ C} \cdot \text{mol}^{-1}$, the electrode area $A = 0.07065 \text{ cm}^2$, the Cr(VI) concentration $C = 2 \times 0.05 = 0.1 \text{ M} = 0.0001 \text{ mol cm}^{-3}$ and a typical aqueous solution kinematic viscosity $\nu = 0.011 \text{ cm}^2 \cdot \text{s}^{-1}$, then the value of $D = 1.13 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ can be obtained for the diffusion coefficient of HCrO_4^- , which is almost identical to that reported in [20] and references therein. The validity of Equation (6) for $n = 3$ is considered as a definitive proof that Reaction (5) takes place quantitatively for sulfuric acid concentrations equal or higher than 0.5 M .

3.4.2. Reticulated Vitreous Carbon (RVC)

Figure 8 presents the results of application constant current electrolysis for 350 mL samples of leachate, containing 5.9 or $3.5 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$, in a small batch reactor under vigorous magnetic stirring. The applied current was 0.5 A which, given the real area of the RVC electrode (see the experimental section), corresponds to a cathode current density of ca. $2.4 \text{ mA} \cdot \text{cm}^{-2}$. The near-linearity of the C vs. t curves implies zero order kinetics. There are three kinetic regimes for the electro-reduction of Cr(VI), i.e., (a) the adsorption of HCrO_4^- (see also the aforementioned discussion of RDE experiments), (b) the electron transfer, and (c) the mass transport. The last two cases are both characterized by 1st-order heterogeneous kinetics. The first one provided that a full monolayer of strongly adsorbed HCrO_4^- is readily formed over a wide concentration range; thus, leading to reactant surface saturation, potentially resulting in reaction rate independent of concentration. This is also implied by the fact that the current efficiency of the process (defined as the charge consumed for Cr(VI) reduction—based on Faraday’s law—divided by the total charge passed) was estimated as 104% and 108% for the two samples. This indicates that, despite the continuous decrease in bulk concentration, the steady-state reduction of a continuously replenished adsorbed layer was able to sustain the applied

current. Noting also that Cr(VI) was converted to Cr(III) by 97.5% in 6 h (for $5.9 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ initial concentration and by 89.8% in 3 h for $3.5 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ initial concentration).

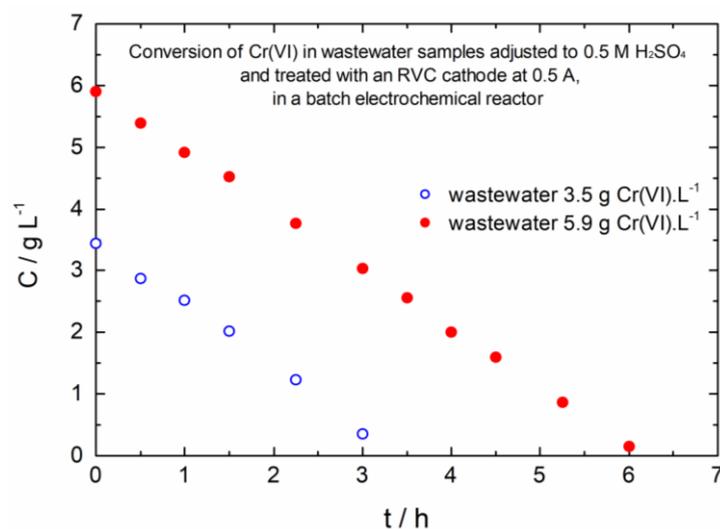


Figure 8. Concentration of Cr(VI) vs. time (h) plots during the electrolysis of 350 mL wastewater samples in a batch reactor, using a reticulated vitreous carbon (RVC) cathode electrode and a constant current of 0.5 A.

Figure 9 presents the results of constant current electrolysis for 800 mL sample of leachate, containing $5.1 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$ in the batch-recirculation reactor arrangement, described in the experimental section. The applied current was 0.5 A which, given the real area of RVC electrode embedded in the plate-and-frame electrochemical cell, corresponds to a cathode current density of ca. $1.25 \text{ mA} \cdot \text{cm}^{-2}$. The shape of the concentration vs. time curves points now to more complicated kinetics (as a plot of $\ln C/C_0$ was not found linear). At the relatively lower flow rates used ($33 \text{ L} \cdot \text{min}^{-1}$), the mass transport limitations are likely to prevail. This is also in line with the overall current efficiency of the process, which is now estimated as only 35%. As the concentration of Cr(VI) in the bulk solution decreases and the mass transport is not sufficient to sustain a full monolayer of adsorbed HCrO_4^- , a competitive reduction process (based on dissolved oxygen reduction, or hydrogen evolution) becomes operative to keep the current constant. The conversion of the Cr(VI) contained in 800 mL of a $5.1 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ wastewater was 99.8% in 36 h.

In order to improve the current efficiency, the batch-recirculation reactor was also operated at constant potential, by selecting the applied potential to be in the range of potentials as recorded during the constant current operation; hence, the value of 3 V was selected. Figure 10 presents the results of constant potential electrolysis at 3 V of an 800 mL sample of leachate, containing $4.1 \text{ g Cr(VI)} \cdot \text{L}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$. The shape of the concentration vs. time curves points again to complicated kinetics (as a plot of $\ln C/C_0$ was not found to be linear). The recorded current started from values at ca. 0.5 A and decreases to less than 0.1 A in 24 h, as expected for a current depending on the concentration of Cr(VI) in the bulk solution, which has been decreasing. Integrating the I vs. t curve (not shown here) a current efficiency of 63% was estimated. The conversion of Cr(VI) from 800 mL leachate sample, containing $4.1 \text{ g} \cdot \text{L}^{-1}$ Cr(VI), was 99.7% in 24 h.

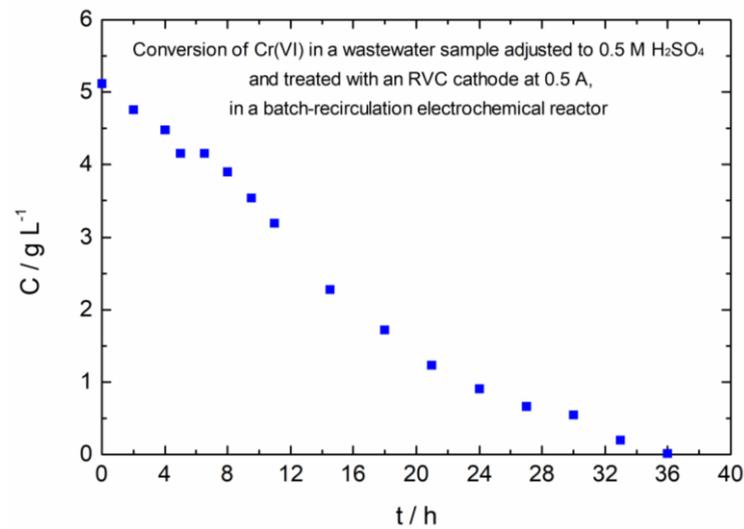


Figure 9. Concentration of Cr(VI) vs. time plots during the electrolysis of a 5.1 g·L⁻¹ leachate samples in a batch-recirculation type reactor, treating 800 mL with a 33 L·h⁻¹ flow rate, using an RVC cathode electrode and a constant current of 0.5 A.

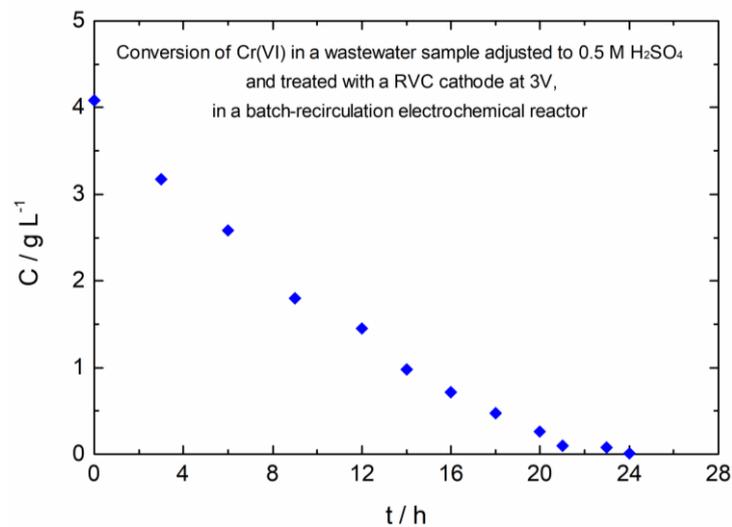


Figure 10. Concentration of Cr(VI) vs. time plots during the electrolysis of 4.1 g·L⁻¹, 800 mL leachate samples in a batch-recirculation type reactor with a 33 L·h⁻¹ flow rate, using an RVC cathode electrode and a constant potential of 3 V.

4. Conclusions

In this study it has been proven that by combining various procedures and exploiting their advantages, it is possible to develop a high-efficiency chromium recovery methodology from tannery sludge. As a first step, the application of thermal treatment can reduce the volume of waste almost by half, albeit oxidizing also the initially present Cr(III) to its toxic Cr(VI) hexavalent form. However, by applying a simple hydrometallurgical acid treatment in the resulting ashes, over 90% of the total Cr content can be extracted, due to Cr(VI) high solubility (the process also being highly selective). Finally, the electrochemical treatment using porous carbon cathodes (RVC), under appropriate sulfuric acid concentration and applied current/potential conditions, can result in a Cr(VI)-to-Cr(III) conversion (reduction) above 95%. The presented methodology highlights the benefits of the circular economy, both environmental and economical, as chromium circulates in a tannery-based route, through its recovery, with minimum losses. As future research, according to the present work, we recommend the clarification of other ions' effect, contained in the leachate,

on the electrochemical treatment and the suitability of reusing the recovered chromium in tanning process.

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