

A Step by Step Investigation of Cr(III) Recovery from Tannery Waste [†]

Evgenios Kokkinos * and Anastasios Zouboulis

Laboratory of Chemical & Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; zoubouli@chem.auth.gr

* Correspondence: kokkinosevgenios@yahoo.gr; Tel.: +306947705980

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Abstract: The effluent of tanneries is a hazardous waste and a combination of physical-chemical and biological techniques is required for its treatment. As a result of the previous processes, a sludge with high chromium content is produced. So, the aim of this study is the hydrometallurgical recovery of chromium in the context of a circular economy. According to chemical characterization, the only form of metal that existed in the sludge was the trivalent, while its content was up to 14.8% w/w. Among the examined acids, the highest efficiency in Cr(III) leaching was achieved by the H₂SO₄ (93%), due to the formation of the soluble CrSO₄⁺. Regarding the step of precipitation, no significant variations were observed between the two alkaline medias that were tested, namely NaOH and Ca(OH)₂.

Keywords: tannery sludge; chromium recovery; hydrometallurgy; circular economy

1. Introduction

Tannery waste treatment is a multi-step process, before it can be safely discharged into a body of water or into the landfill or reused. The goal is to reduce or remove organic load, solids, nutrients, chromium and other pollutants, as each recipient can accept specific amounts of them without being degraded. In order to reduce emissions, tannery waste treatment is mandatory, by a suitable combination of physical-chemical and biological techniques, inside and/or outside the facility [1].

Technologies that have been studied for chromium recovery from tannery wastewater include flocculation, chemical precipitation [2], adsorption [3,4], ion exchange resins [5], membrane use [6], and electrochemistry [7], as well as bioaccumulation in algae [8]. However, the high cost, fixed and operational, combined with the low efficiency and selectivity, make their application in the field unprofitable. Often, in order to optimize efficiency, the combination of two or more technologies was considered, resulting in additional cost increase [9,10]. The main technology used for tannery wastewater treatment is precipitation/flocculation; despite the fact that it has the lowest selectivity, it is a low cost and high efficiency technology in removing pollutants from the aqueous phase. Of course, it comprises the final stage of a typical tannery waste treatment plant, which produces a chromium-rich sludge.

The aim of this study is chromium recovery from the abovementioned tannery sludge by the principals of hydrometallurgy. Such a process consists of two steps—metal leaching from the sludge using an acidic media and then its precipitation using an alkaline media, in order to produce Cr(III) in a solid phase, which will be re-fed to tanneries.

2. Materials and Methods

2.1. Tannery Sludge

As a reference sample, we obtained tannery air-dried sludge from the central wastewater treatment plant (Figure 1) that serves the respective enterprises in the main industrial area of Thessaloniki (Sindos—Northern Greece). The initial sludge was ground and sieved (<0.5 mm), in order to be homogenized.



Figure 1. Air dried tannery sludge obtained from the respective wastewater treatment plant.

2.2. Sample Characterization

The chemical characterization was conducted by acid digestion, as required for the specific sample. In particular, 0.5 g of fine 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. Contrary to the standard procedure, this was not followed by the addition of concentrated HCl, as in that case a significant portion of the hexavalent chromium, if contained in the sludge, would be reduced to its trivalent form. The major metals (Cr, Ca, Mg etc.) were determined by flame atomic absorption spectrophotometry, using a Perkin-Elmer AAnalyst 800 instrument [11], and Cr(VI) by the standard 1,5-diphenylcarbazide method, using a Hitachi U-2000 spectrophotometer at 540 nm [12]. The organic matter content and organic carbon were measured by the TOC-VCSH E200V Shimadzu TOC analyzer [13].

2.3. Hydrometallurgical Experiments

The leaching of chromium from the sample was conducted following the hydrometallurgical principals by applying various acidic medias. In a beaker was placed 1 g of the sample and the leaching media. The examined acids were HCl, HNO_3 and H_2SO_4 , in the concentration range 0.02–2 N. The rest of the experimental conditions remained stable: contact time at 60 min, temperature at 25 °C and liquid-to-solid ratio (L/S) equal to 25. After the extraction stage, the liquid phase separated by filtration under vacuum and the major metals concentration (namely Cr and Ca) were determined in the filtrate. The precipitation step was applied in the filtrate, using NaOH and $\text{Ca}(\text{OH})_2$ as alkaline medias, in the pH range of 6–9.5. In detail, 25 mL of chromium leachate was placed in a beaker and the desired pH was adjusted by adding the alkaline media dropwise, under stirring conditions. When the system reached equilibrium, stirring continued for an extra hour.

3. Results and Discussion

3.1. Sample Characterization

Through chemical characterization (Table 1), it was proven that tannery sludge contained a high amount of Cr(III) (14.1%), while the complete absence of the toxic Cr(VI) was confirmed. In addition, an equally high content was observed for Ca (14.8%), due to the usage of corresponding

reagents during the tannin process. On the other hand, due to the nature of the raw material (leather), the organic matter was also high (22%). Other metals worth mentioning were Mg, Na, Al and Fe (<2.5%), but in any case their percentage in the sludge was much lower than the previous ones.

Table 1. Chemical composition of tannery sludge.

Cr(III)	Cr(VI)	Ca	Mg	Na	Al	Fe	OM
% w/w							
14.1	ND	14.8	2.4	1.5	0.5	0.46	22

3.2. Leaching of Cr(III)

Hydrometallurgical recovery of Cr(III) from the tannery sludge mainly requires its leaching by an acidic media. When the three common acids (usually applied to these types of experiments) were examined, significant deviations were observed regarding their efficiency. As shown in Figure 2a, the maximum percentage of Cr(III) extraction (93%) was obtained by using 1 N H₂SO₄, compared with similar concentrations of HNO₃ (73%) or HCl (65%). It is also noted that by increasing the acid's concentration (normality), no further improvement in the extraction was found.

The leaching results are attributed to the solubility of the Cr(III) forms, as shown by the data extracted by the specialized software Visual MINTEQ version 3.1, according to which different chromium forms were obtained, using the experimental conditions of the present study. Although the CrNO₃²⁺ mode exhibits higher solubility than CrSO₄⁺ or CrCl₂⁺, the equilibrium conditions (i.e., pH, Cr and acid concentration) did not favor their formation [14]. In any case, the dominant species was the Cr³⁺ ion, but when 1 N H₂SO₄ was applied, about 16% of the total amount of chromium was obtained as CrSO₄⁺, which has higher solubility than Cr³⁺. The latter was the only species when 1 N HNO₃ was applied. Finally, 1 N HCl caused 44% formation of CrCl₂⁺, which is the least soluble mode [15].

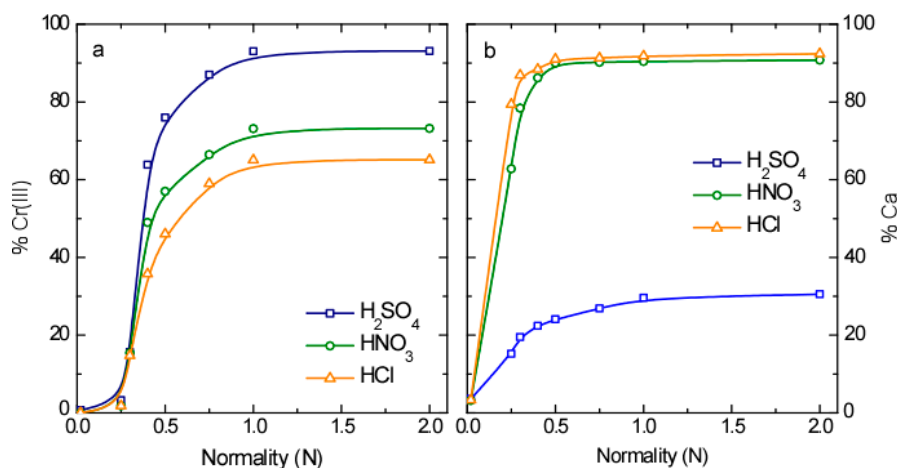


Figure 2. Cr(III) (a) and Ca (b) extraction from tannery waste by the use of different acids, applied in different (initial) concentrations.

3.3. Selectivity

Since tannery sludge contains an even higher amount of calcium than chromium, its behavior was examined during the hydrometallurgical extraction with respect to the method's selectivity. Figure 2b shows the percentage of Ca leached under the same conditions as before, i.e., Cr(III) recovery. When HNO₃ and HCl were applied, the leaching of Ca was extremely high (~90%), due to the high solubility of its forms in the primary waste. In contrast, when H₂SO₄ was applied, only a small portion of Ca was leached (~30%), due to the formation of the insoluble in acidic media CaSO₄ [16], according to software Visual MINTEQ.

3.4. Precipitation

In the process of recovering chromium from tannery sludge, the last and necessary step is precipitation. The experimental process was based on the low solubility of Cr(III) and hence its precipitation by increasing the leachate's pH. The two tested reagents were $\text{Ca}(\text{OH})_2$ and NaOH , the most economical and widely used. The leachate had an initial concentration of 5.2 g Cr(III)/L, as obtained using 1 N H_2SO_4 for 1 h at 20 °C and a L/S ratio equal to 25.

According to Figure 3, almost the entire amount of Cr(III) was precipitated for pH values above 7 (<98%), and it separated from the aqueous phase. On the other hand, the efficiency was dramatically decreased for pH values below 7, especially when the NaOH was applied. The deviation between the two examined alkaline reagents was attributed to their chemical properties. Calcium is less soluble than sodium [14], so by following a co-precipitation mechanism, the less soluble Cr(III) remained by applying $\text{Ca}(\text{OH})_2$. In addition, $\text{Ca}(\text{OH})_2$ is a weaker base than NaOH , and therefore a proportionally higher amount was required for the desired pH adjustment. As a result, the corresponding precipitates differed both in color and volume (Figure 4). The chemical characterization of the precipitates, as obtained by applying the optimum conditions (pH 8), revealed that the use of NaOH had higher Cr(III) content (31%) than $\text{Ca}(\text{OH})_2$ (7.5%). Instead, Ca content had the opposite behavior (3.8% and 17%, respectively).

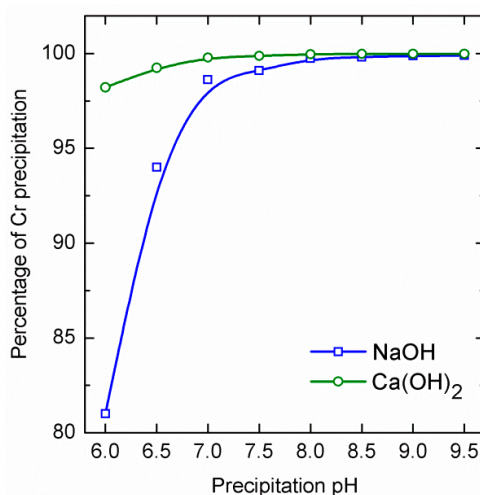


Figure 3. Percentage of Cr(III) precipitation by applying $\text{Ca}(\text{OH})_2$ and NaOH , in various pH.

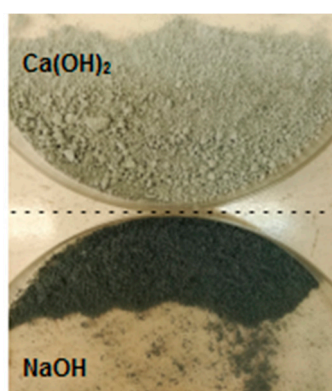


Figure 4. Precipitates by adding $\text{Ca}(\text{OH})_2$ and NaOH into the chromium's leachate, as obtained by using 1 N H_2SO_4 .

4. Conclusions

In this research, it was proved that chromium recovery from the air-dried tannery sludge is possible, promoting the sustainable management of this industrial waste. In particular, Cr(III) was leached by H₂SO₄ directly from the initial waste with high selectivity against the co-existing higher amount of Ca. Afterwards, by increasing the leachate's pH with NaOH, a chromium-rich precipitate was obtained that can be fed back to the corresponding enterprises as a raw material.

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Conflicts of Interest: The authors declare no conflict of interest.

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