A step by step investigation of Cr(III) recovery from tannery waste

Evgenios Kokkinos * and Anastasios Zouboulis

Department of Chemistry, Aristotle University of Thessaloniki, Greece
* Correspondence:kokkinosevgenios@yahoo.gr; Tel.: +306947705980

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, aim of this study is the hydrometallurgical recovery of chromium in the context of circular economy. According to chemical characterization the only metal's form 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 achieved by the H_2SO_4 (93%), due to the formation of the soluble $CrSO_4^+$. Regarding the step of precipitation, no significant varions were observed between the two alkaline medias that 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 will be safely discharged into a body of water or into the landfield 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 mantadory, 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 are flocculation, chemical precipitation [2], adsorption [3; 4], ion exchange resins [5], membrane use [6], 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 consists the final stage of a typical tannery waste treatment plant, which produces a chromium rich sludge.

Aim of this study is chromium recovery from the above mentioned tannery sludge by the principals of hydrometallurgy. Especially, such a process consisted by two steps, metal's leaching from the sludge using an acidic media and then its presipitation using an alkaline media, in order to be produced Cr(III) in a solid phase, which will be re-fed to tanneries.

2. Materials and Methods

2.1. Tannery sludge

As reference sample obtained tannery air dried sludge from the central wastewater treatment plant (Fig. 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 conducted by acid digestion, required for the specific sample. In particular, 0.5 g of fine powder 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 contrary to the standard procedure, it was not followed by the addition of concentrated HCl, as in that case a significant portion of the hexavalent chromium, if it 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, organic carbon was measured by the TOC-VCSH E200V Schimadzu 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 $Ca(OH)_2$ as alkaline medias, in the pH range of 6-9.5. In detail, 25 mL of chromium's leachate was placed in a beaker and the desired pH was adjusted be 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 characterizatrion (Table 1), it was proven that tannery sludge conteined a high amount of Cr(III) (14.1%), while the complete absence of the toxic Cr(VI) was confirmed. In addition, equally high content 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), organic matter was also high (22%). Other metals worth to be mentioned were Mg, Na, Al and Fe (<2.5%), but in any case their percentage in the sludge were extremely 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 1N H_2SO_4, compared with similar concentrations of HNO_3 (73%) or HCl (65%). It is also noted that by increasing acid's concentration (normality), no further improvement in the extraction was found.

The leaching results were attributed to the solubility of the Cr(III) forms, 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 $CrNO_3^{2+}$ mode exhibits higher solubility than $CrSO_4^+$ or $CrCl_2^+$, the equilibrium conditions (i.e. pH, Cr and acid concentration) did not favor their formation [14]. In any case, the dominant specie was the Cr^{3+} ion, but when 1N H_2SO_4 was applied, about 16% of the total amount of chromium was obtained as $CrSO_4^+$, which has higher solubility than Cr^{3+}. The latter was the only species when 1N HNO_3 was applied. Finally, 1N HCl caused 44% formation of $CrCl_2^+$, which is the least soluble mode [15].

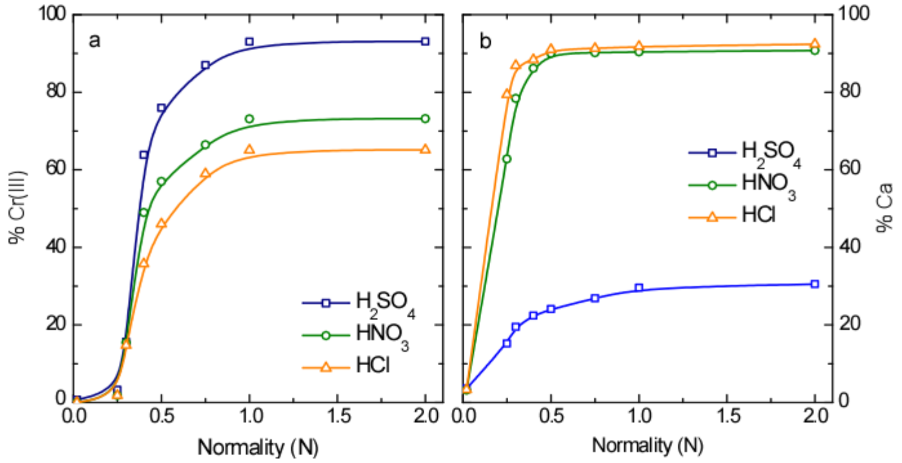

Figure 2. Cr(III)–(a) and Ca–(b) extraction from tannery waste by the use of different acids, applied in different (initial) concentrations.

3.3. Selectivity

Since tannery sludge contains even higher amount of calcium than chromium, its behavior was examined during the hydrometallurgical extraction with respect to method's selectivity. Figure 2b shows the percentage of Ca leached under the same conditions as before, i.e. Cr(III) recovery. When HNO_3 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 H_2SO_4 was applied, only a small portion of Ca was leached (~30%), due to the formation of the insoluble in acidic media $CaSO_4$ [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 leachates pH. The two tested reagents were $Ca(OH)_2$ and NaOH, the most economical and widely used. The leachate had an initial concentration of 5.2 g Cr(III)/L, as obtained using 1N H_2SO_4 for 1 hour at 20° C and a L/S ratio equal to 25.

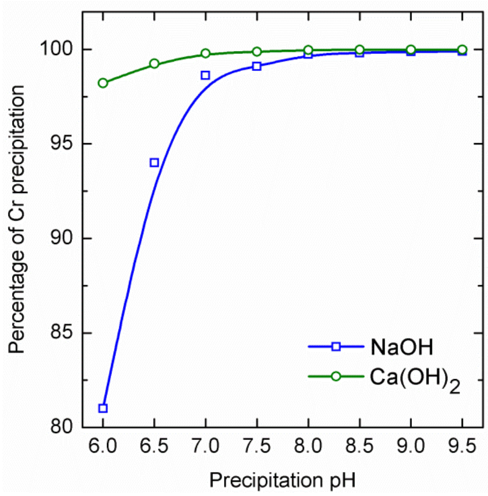

Figure 3. Percentage of Cr(III) precipitation by appling $Ca(OH)_2$ and NaOH, in various pH.

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, less solable Cr(III) remained by appling $Ca(OH)_2$. In addition, $Ca(OH)_2$ is a weaker base than NaOH, therefore a proportionally higher amount was required for the desiered pH adjustment. As a result, the corresponding precipitates differed both in color and volume (Fig. 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 $Ca(OH)_2$ (7.5%). Instead, Ca content had the opposite behavior (3.8% and 17%, respectively).

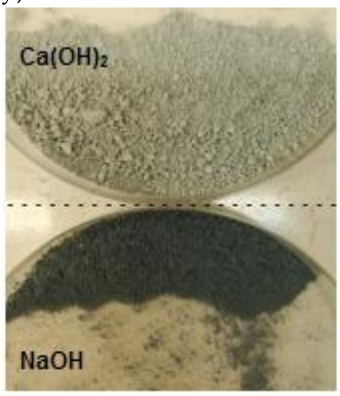

Figure 4. Precipitates by adding $Ca(OH)_2$ and NaOH into the chromium's leachate, as obtained by using 1N H_2SO_4.

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. Especially, Cr(III) was leached by H_2SO_4 directly from the initial waste with high selectivity against the co-existing higher amount of Ca. Afterwords, by increasing the leachates pH with NaOH, a chromium-rich precipitate was obtained, that it can be fed back to the corresponding enterprises, as a raw material.

Acknowledgments: We acknowledge support of this work by the project "INVALOR: Research Infrastructure for Waste Valorization and Sustainable Management" (MIS 5002495) which is implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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

References

1. United Nations Industrial Development Organization (UNIDO), Introduction To Treatment of Tannery Effluents, What Every Tann. Should Know about Effl. Treat., Vienna, 2011.
2. Guo, Z.R., Zhang, G., Fang, J., Dou, X. Enhanced chromium recovery from tanning wastewater. J. Clean. Prod. 2006, 14, 75-79, https://doi.org/10.1016/ j.jclepro.2005.01.005.
3. Dahbi, S., Azzi, M., Saib, N., De la Guardia, M., Faure, R., Durand, R. Removal of trivalent chromium from tannery waste waters using bone charcoal. Anal. Bioanal. Chem. 2002, 374, 540–546, https://doi.org/10.1007/s00216-002-1490-9.
4. Hintermeyer, B.H., Lacour, N.A., Perez Padilla, A., Tavani, E.L. Separation of the chromium(III) present in a tanning wastewater by means of precipitation, reverse osmosis and adsorption. Lat. Am. Appl. Res. 2008, 38, 63–71.
5. Sahu, S.K., Meshram, P., Pandey, B.D., Kumar, V., Mankhand, T.R. Removal of chromium(III) by cation exchange resin, Indion 790 for tannery waste treatment. Hydrometallurgy 2009, 99, 170–174, https://doi.org/10.1016/j.hydromet.2009.08.002.
6. Cassano, A., Molinari, R., Romano, M., Drioli, E. Treatment of aqueous effluents of the leather industry by membrane processes: A review. J. Memb. Sci. 181 2001, 111-126, https://doi.org/10.1016/S0376-7388(00)00399-9.
7. Sirajuddin, Kakakhel, L., Lutfullah, G., Bhanger, M.I., Shah, A., Niaz, A. Electrolytic recovery of chromium salts from tannery wastewater. J. Hazard. Mater. 2007, 148, 560–565, https://doi.org/10.1016/j.jhazmat.2007.03.011.
8. Aravindhan, R., Madhan, B., Rao, J.R., Nair, B.U., Ramasami, T. Bioaccumulation of Chromium from Tannery Wastewater: An Approach for Chrome Recovery and Reuse. Environ. Sci. Technol. 2004, 38, 300–306, https://doi.org/10.1021/es034427s.
9. Fabiani, C., Ruscio, F., Spadoni, M., Pizzichini, M. Chromium(III) salts recovery process from tannery wastewaters. Desalination 1997, 108, 183–191, https://doi.org/10.1016/S0011-9164(97)00026-X.
10. O'Dwyer, T.F., Hodnett, B.K. Recovery of chromium from tannery effluents using a redox–adsorption approach. J. Chem. Technol. Biotechnol. 1995, 62, 30–37, https://doi.org/10.1002/jctb.280620105.
11. Alpha, Water Environment Federation, American Water Works Association, Standard Methods for the Examination of Water and Wastewater (Part 4000-6000), Stand. Methods Exam. Water Wastewater., 1999. ISBN 9780875532356.
12. US EPA, Method 7196A for Chromium, Hexavalent (colorimetric), US EPA Method 7196A, 1992.
13. EN 13137, Chemical Analyses - Determination of total organic carbon (TOC) in waste, sludges and sediments, Draft European Standard, 2004.
14. D.R. Lide, CRC Handbook of Chemistry and Physics, Internet Version 2005, CRC Press, Boca Raton, FL, 2005.
15. Kokkinos, E., Proskynitopoulou, V., Zouboulis, A. Chromium and energy recovery from tannery wastewater treatment waste: Investigation of major mechanisms in the framework of circular economy. J. Environ. Chem. Eng. 2019, 7, 103307, https://doi.org/10.1016/j.jece.2019.103307.
16. Shen S.B., Tyagi, R.D., Blais, J.F. Extraction of Cr(III) and other metals from tannery sludge by mineral acids. Environ. Technol. 2001, 22, 1007-1014, http://dx.doi.org/10.1080/09593332208618216.