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Hydrometallurgical Recovery of Cr(III) from Tannery Waste: Optimization and Selectivity Investigation

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Abstract: Tanneries produce significant quantities of hazardous waste/waters and, according to international environmental organizations, their further recycling/reuse/exploitation in the context of circular economy is considered mandatory. A relevant case study is the recovery of Cr(III), used in large amounts during the tanning process, which can be recovered from the corresponding industrial waste/sludge. The aim of this work is to optimize the Cr(III) hydrometallurgical recovery from the tannery sludge by examining the major experimental conditions that affect the efficiency of its different sequential steps, namely extraction/leaching and precipitation. The chemical characterization revealed that tannery sludge contains high amounts of Cr(III) (14.1%), Ca (14.8%), and organic matter (22%). The extraction of Cr(III) was examined by applying various common acids (H_2SO_4 , HNO_3 , HCl) in the concentration range of 0.02–2 N. The highest selectivity and efficiency (93%) were obtained by the addition of H_2SO_4 as the insoluble CaSO_4 and soluble CrSO_4^+ species were formed. Regarding the experimental conditions, only the increase in temperature showed a positive effect on Cr recovery. The Cr(III) can be further precipitated from the resulting leaching solution by increasing the equilibrium pH; the precipitate with the higher purity in $\text{Cr}(\text{OH})_3$ (70%) was obtained by the application of NaOH and could possibly be reused by tanneries.

Keywords: tannery waste management; chromium(III) recovery; hydrometallurgy

1. Introduction

Tanning is the treatment of animal skin/hide to acquire specific properties, such as strength and elasticity, and to be eventually transformed to leather. The predominant tanning technology is mainly based on the use of Cr(III) salts (chrome tanning), whereas when using reagents of plant origin (e.g., tannins), leather of the same high quality cannot be produced (i.e., “vegetable” tanning). Due to the nature of raw materials and the use of several chemical reagents commonly applied during the tanning process, tanneries produce hazardous wastewaters containing high concentrations of residual chemicals (not used by the process). Several international environmental organizations (e.g., UNEP etc.), recognizing the need for sustainable options in waste management, promote the exploitation of these wastes through the recovery of useful by-products, with emphasis given mainly to high chromium content, in the context of the circular economy [1].

In general, the selective recovery of metals from wastewaters has been tested by various technologies, with the most common among them being adsorption [2] and membranes [3]. Examples of technologies being studied especially for the recovery of chromium directly from the tannery wastewaters are chemical precipitation [4,5], adsorption [6,7], ion exchange resins [8], filtration [9,10], electrochemistry [11,12], and bioaccumulation [13]. However, the relatively high cost of most of these methods, combined with the low efficiency and selectivity issues, make their industrial application

quite problematic. Often, in order to optimize efficiency, the combination of two or more technologies has been considered, resulting in an additional increase in cost [14,15].

On the other hand, as tannery wastewaters are recognized as hazardous, their appropriate treatment is considered mandatory. The dominant methodology consists of a suitable physicochemical and biological technique combination, inside and/or outside the industrial facility [16]. Despite the fact that this treatment process has low selectivity, it is considered a low-cost and high-efficiency technology, removing the majority of pollutants from the aqueous phase before being discharged into the receiving waters or retreated appropriately (according to the achieved effectiveness), or even reused by the tannery. It should be noted that the main purpose is to mainly reduce or remove the organic load, solids, nutrients, and chromium, as well as any other possibly co-existing pollutants [17]. As a result of the aforementioned treatment methodology, the corresponding treatment plants produce a chromium-rich sludge, which presents a high potential for chromium recovery and potential reuse.

The most widespread technology used to recover metals from sludges (as well as from contaminated soils, or from poor minerals) is hydrometallurgy, aiming to successfully separate the desired constituents while reducing the waste residual volume left for final disposal [18]. The treated sludge residue may be subsequently applied safely, e.g., to agricultural land, disposed of in landfills, or even further processed, according to its specific properties and the respective legislation/permission. Relevant methods, as suggested by the respective literature, for the treatment of tannery sludge and recovery of Cr(III) are chemical extraction [19,20], bio-extraction (with the application of microorganisms) [21,22], electro-kinetic extraction [23], and supercritical fluid extraction [24]. It should be noted, however, that their yield may vary widely as they depend on various parameters, such as appropriate sludge pretreatment and composition, and metal concentrations (and speciation), as well as the applied leaching/extraction conditions.

This work aims for the optimal recovery of Cr(III) from a typical tannery sludge, produced by the treatment of wastewaters from the tanning industry, by applying the basic principles of hydrometallurgy. In our previous relevant study [25], a thorough investigation of the major mechanism during this process was conducted, which was the trigger for the further optimization of Cr(III) recovery efficiency and, at the same time, the maximization of the respective selectivity issues. As the applied technology includes two subsequent steps, i.e., extraction/leaching and precipitation, these were optimized separately in order to produce a suitable final solid with high content and purity, regarding Cr(III), which could be fed back and reused in the tanning as an appropriate chemical. In addition, the results will provide an interpretation of how the experimental conditions and the composition of this waste may affect the efficiency of recovery, addressing, along with the chemical and structural characterization of the produced precipitate/reagent, a fundamental gap in the respective literature.

2. Materials and Methods

2.1. Tannery Sludge

The examined tannery sludge was obtained from the central wastewater treatment plant of a tannery cluster in the main industrial area of Thessaloniki (Sindos-Northern Greece). The initial sludge was air-dried, ground, and sieved (<0.5 mm) to achieve homogenization.

2.2. Leaching Experiments

Extraction of Cr(III) from the tannery sludge was conducted, following the fundamentals of the hydrometallurgical approach, i.e., by applying various inorganic acids. More specifically, in a glass beaker, 1 g of the pretreated industrial sludge and the respective extraction/leaching media were placed. The examined acids were HCl, HNO₃, and H₂SO₄, examined in the concentration range of 0.02–2 N. Other experimental conditions, also investigated to optimize the process, were the contact time (30–120 min), temperature (20–60 °C), and liquid-to-solid ratio (L/S) (10–50). After the extraction step, the liquid phase was separated by filtration under vacuum and the major parameters were

determined in the filtrate, namely the concentrations of Cr, Ca, and organic carbon, by flame atomic absorption spectrophotometry (FAAS), a Perkin-Elmer Analyst 800 instrument, and a Shimadzu Total Organic Carbon analyzer model TOC-VCSH E200V, respectively.

2.3. Precipitation Experiments

The precipitation step for Cr(III) recovery was subsequently applied to the resulting (from the previous step) leachate/filtrate solution, obtained by the optimal experimental conditions. Then, 25 mL of the aforementioned solution was placed in a beaker, followed by stirring. The pH was then adjusted to various values within the range of 6–9.5 by the dropwise addition of an alkaline solution. NaOH and Ca(OH)₂ solutions (1 N) were the examined alkaline reagents. When the system reached equilibrium (~1 h), it was left under stirring conditions for an extra hour (aiming to age/mature the produced precipitate).

2.4. Precipitate Characterization

The produced precipitate was collected by filtration, dried, and ground to achieve homogenization. Cr(III) and other major substances (Ca, organic carbon (OC), etc.) were determined (after appropriate acid digestion) by the FAAS and TOC analyzer, as before. In particular, 0.1 g of the precipitate's dry powder was placed in a 100 mL PTFE beaker with 20 mL of concentrated HNO₃ and refluxed on a heated source at 95 °C for 24 h. The major structural crystalline phases were also identified by the application of 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.

3. Results and Discussion

3.1. Tannery Sludge Characterization

A thorough physicochemical and structural characterization of the examined tannery sludge was previously published [25]; therefore, only a brief outline is described in the following. The corresponding composition is presented in Table 1, where the high Cr(III) content was proven, as well as the absence of other chromium forms, namely of Cr(VI). The presence of a significant amount of organic carbon was attributed to the composition and treatment/tanning of the raw material (i.e., animal skin). By contrast, the existence of inorganic carbon was due to the formation of CaCO₃, noting that the Ca percentage was found almost as high as Cr(III). Other identified phases/forms of calcium were Ca(OH)₂ and CaSO₄. Mg was also presented with a noticeable content (2.5%), which, however, is an order of magnitude lower than those of the cases with Ca and Cr presence. Other metals, such as Fe, Al, Zn, etc., were measured with much lower contents (<0.5%) in the initial waste, and they are not considered capable to significantly influence the applied hydrometallurgical/selective leaching procedure. In addition, tannery sludge was proved to be a strongly alkaline material, while the quantification of leachable ions was determined by the measurement of electrical conductivity.

Table 1. The main components and physicochemical parameters of tannery sludge [25].

Moisture	Organic Carbon	Inorganic Carbon	Ca	Cr(III)	Mg	pH	Conductivity
		%					mS/cm
11	12.2	3.1	14.8	14.1	2.4	9.1	0.96

3.2. Extraction/Leaching of Cr(III)

The efficiency of Cr(III) extraction from tannery sludge was investigated by applying the most common inorganic acids in hydrometallurgy, namely HCl, HNO₃, and H₂SO₄. Figure 1a shows the percentage of the metal's leaching, noting that up to a concentration of 0.3 N, all acids presented a similar yield. As this process highly depends on the solubility of Cr(III) in the aqueous phase, a

portion of the added acids was initially consumed in order to neutralize the existing alkaline ions of the sludge, which have also been leached, as indicated by the physicochemical characterization of the produced leachate (i.e., pH 9.1 and electrical conductivity 0.96 mS/cm) [25]. Beyond this concentration value (0.3 N), the percentage leaching of Cr(III) increased rapidly and notable variances between the examined acids were observed. The best performance was shown by H₂SO₄, resulting in an extraction of 93% Cr(III). In contrast, HNO₃ (73%) and HCl (65%) showed substantially lower yields. Although the dominant metal's form was the simple ionic (Cr³⁺) species for all cases, a part of them may form complexes, depending on the applied acid. Therefore, the aforementioned deviations, regarding Cr(III) extraction, can be attributed to the formation of more soluble CrSO₄⁺ species (Figure S1), as compared to the formation of Cr³⁺ species in the case of HNO₃ (Figure S2) and with CrCl²⁺ species in the case of HCl (Figure S3). It was also clarified that the formation of even more soluble CrNO₃²⁺ species did not occur.

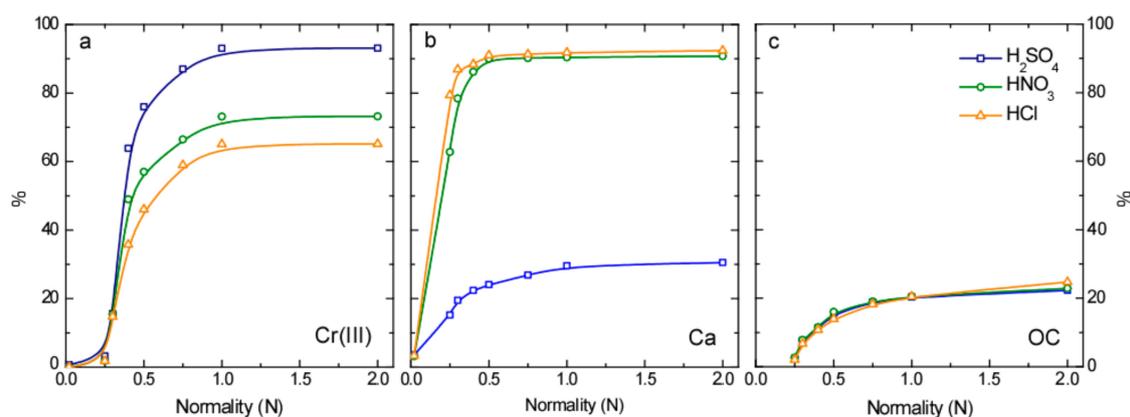


Figure 1. (a) Cr(III), (b) Ca, and (c) organic carbon (OC) leachability from the tannery sludge when using three common inorganic acids; experimental conditions: 20 °C, 60 min, and liquid-to-solid ratio (L/S) equal to 25 [25].

3.3. Selectivity

Considering the selectivity of the applied extraction method, i.e., the selective extraction of Cr(III) against the other co-existing major components, namely that of Ca and of organic carbon (OC), their behavior during the extraction step was further investigated. Figure 1b,c present their leaching efficiency under the same experimental conditions as previously described. Especially, with the application of HNO₃ and HCl, an extraction yield over 90% for Ca was reached due to the high solubility of the respective Ca forms in the tannery sludge, which are mainly CaCO₃ and Ca(OH)₂. Instead, the formation of the insoluble (in acidic media) CaSO₄ was favored when H₂SO₄ was applied and, therefore, the corresponding Ca extraction in this case was found lower than 30% [26]. Regarding OC, no variations between the examined acids were observed (Figure 1c), while the maximum leaching efficiency was slightly over 20%. This was attributed to the partially dissolved organic matter content of tannery sludge during the applied mild acidic conditions.

3.4. Effect of Major Experimental Conditions

Besides the acid and its concentration, the other (major) experimental parameters affecting the yield of extraction/leaching in hydrometallurgy are contact time, temperature, and liquid-to-solid ratio (L/S). Therefore, the Cr, Ca, and OC behavior during the leaching process was investigated under various conditions/values of these parameters by using the addition of 0.4 N H₂SO₄ in these experiments.

Regarding the contact time, it can be concluded from Figure 2a that the system required at least 60 min in order to reach equilibrium. In addition, doubling this time showed only a slight increase in Cr(III) leaching efficiency (~4%), while Ca and OC concentrations were found to be relatively stable.

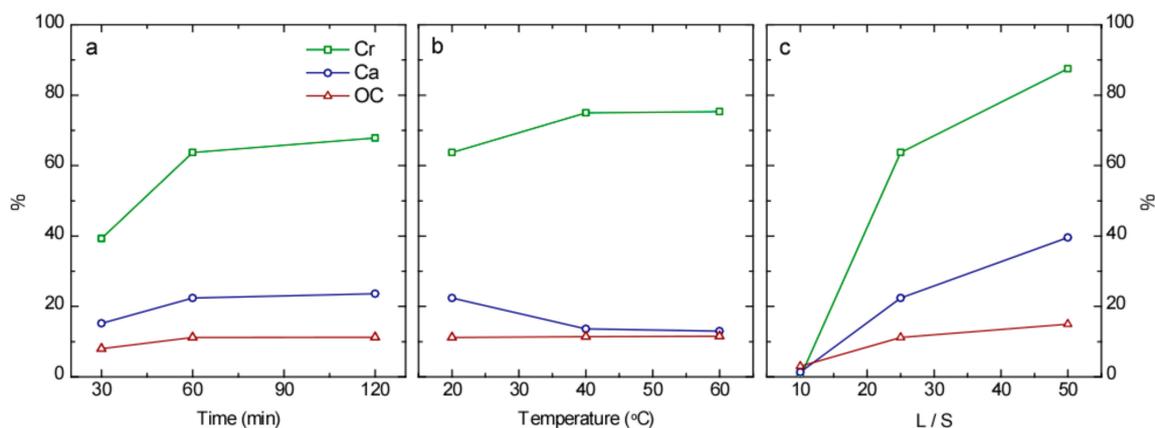


Figure 2. (a) Cr(III), (b) Ca, and (c) organic carbon (OC) leachability from tannery sludge under various experimental conditions (i.e., contact time, temperature, L/S/ ratio) by applying 0.4 N H₂SO₄.

In order to investigate the effect of temperature, higher values than those applied during the preliminary evaluation experiments (20 °C) were examined, producing different results, regarding the components of interest (Figure 2b). The Cr(III) extraction rate at 40 °C showed an increase of around 10% while remaining stable at 60 °C. This was attributed to the inter-dependence between solubility and temperature as they are proportional. A similar behavior was expected for Ca, but from the slight decrease in leaching percentage (~5%), it can be concluded that the increase in temperature in this case has favored the formation of insoluble CaSO₄. In particular, the solubility of this component is an exothermic reaction; thus, by increasing the temperature, Ca remained mainly in the solid phase [27]. On the contrary, OC leachability was unaffected by the increase in temperature and remained constant for the examined temperature range.

According to Figure 2c, the L/S value is an important parameter of this process. For a ratio equal to 10, it appeared that the extraction rate of all investigated components was near zero. By increasing this value to 25, a sharp increase in performance was noticed. A further increase to 50 resulted in a significant Cr(III) leaching efficiency (~90%), but at the same time, the selectivity of the process reduced because the extraction of Ca and OC also increased. Therefore, careful evaluation of the L/S ratio, as well as of the contact time, should be performed, also considering the unavoidable dissolution of the other co-existing components. Especially, for the case of Ca, the increase in leaching was much higher between the values of L/S ratios of 25 and 50, as compared to the corresponding increase in Cr(III) leaching, creating problems in the selectivity process.

3.5. Precipitation

In the hydrometallurgical recovery of Cr(III) from tannery sludge, the next step is to precipitate the metal from the leaching solution. This step was intended to selectively precipitate Cr(III) as Cr(OH)₃, due to its low solubility, by increasing the pH of the produced leachate/filtrate through the addition of an appropriate alkaline reagent. The examined alkaline media in this case were NaOH and Ca(OH)₂, i.e., the most widely used and of relatively lower cost, noting that the leachate/filtrate contained an initial concentration of 5.2 g Cr(III)/L, as resulted by the application of 1 N H₂SO₄ for 1 h at 20 °C and S/L equal to 25.

From Figure 3, it was revealed that almost the entire amount of Cr(III) was precipitated and separated as solid (Cr(OH)₃) from the solution. The process efficiency exceeded 99% for pH values >7, and no significant differences between the two reagents were observed, taking into account the high initial Cr(III) concentration. Furthermore, the resulting aqueous phase (after the separation of the produced solids by filtration) did not meet the criteria for direct disposal in a water body (as the respective concentration limit imposed by legislation is 0.3 mg Cr_{total}/L) [28]. Instead, it can be disposed of in a wastewater treatment plant for further treatment, which can be realized for pH values

≥ 8 ; e.g., at pH 8, dissolved chromium is 2.4 mg/L for the case of NaOH addition and 2 mg/L in the case of $\text{Ca}(\text{OH})_2$ addition, with respect to the method's efficiency and sustainability, noting also that the higher permissible (by legislation) concentration limit in this case is 2.5 mg $\text{Cr}_{\text{total}}/\text{L}$ [29]. On the contrary, in the pH range of 6–7, the efficiency was found to substantially decrease and the residual (dissolved) metal concentration was found to increase up to two orders of magnitude (e.g., at pH 6, it is 345 mg/L in the case of NaOH and 134 mg/L in the case of $\text{Ca}(\text{OH})_2$). The significant differences between the examined alkaline reagents were attributed to a co-precipitation mechanism between Cr(III) and Ca, because Ca presents substantially lower solubility as compared to Na [30].

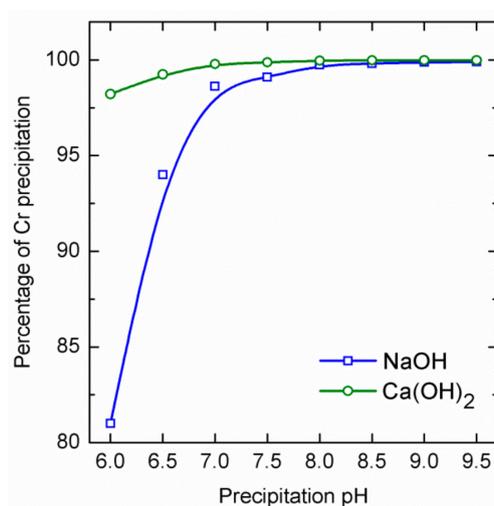


Figure 3. Cr(III) precipitation by applying common alkaline reagents at various equilibrium pH values.

3.6. Precipitate Characterization

The chemical composition of the produced precipitates, by using the examined alkaline reagents, is presented in Figure 4. It was concluded that the application of NaOH resulted in a Cr(III)-rich precipitate (up to 35.5%), while the other components remained at much lower percentages in any equilibrium pH value (i.e., <5%). Moreover, NaOH was also a source of Na, resulting in small amounts of it in the produced precipitate, although it was not actually contained in the initial sludge. On the other hand, the use of $\text{Ca}(\text{OH})_2$ resulted in a substantial increase in Ca content compared to the theoretical/expected, according to the concentration in the filtrate, as it was a respective source of calcium and a corresponding decrease in chromium (around 7%). This was attributed to the addition of a proportionally higher $\text{Ca}(\text{OH})_2$ amount for pH adjustment, as it is a weaker alkaline agent when compared to NaOH. In addition, as aforementioned, Ca is less soluble than Na; therefore, a higher volume of solids was obtained by precipitating the same amount of Cr(III).

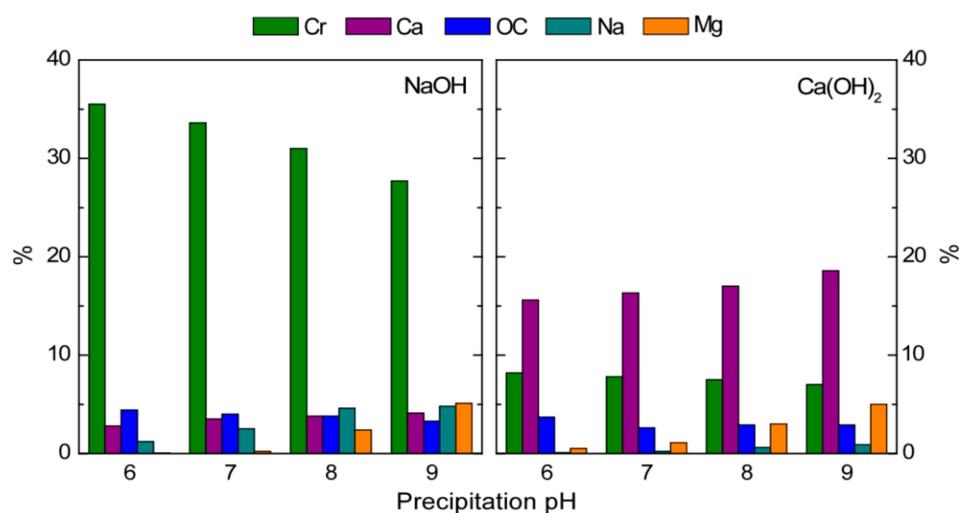


Figure 4. Major components of the examined precipitates by applying common alkaline reagents.

According to the XRD spectra of the precipitates (Figure 5), the main structural phase was the hydroxylated forms of Cr(III) when NaOH was used as alkaline media. This result was concluded through its characteristic amorphous structure, which was reflected in the spectra as noise [31]. The few peaks that formed are attributed to sulfates, such as Na_2SO_4 (JCPDS card No. 74-1738) and CaSO_4 (JCPDS card No. 74-1905), but without a complete identification. In the precipitates obtained by the addition of $\text{Ca}(\text{OH})_2$, the dominant phase was CaSO_4 due to its high content and crystallinity. Specifically, $\text{CaSO}_4(\text{H}_2\text{O})_2$ peaks (JCPDS card No. 74-1905) were observed at all pH values, whereas for the values of 8 and 9, peaks of $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$ were additionally found (JCPDS card No. 81-1848) [32].

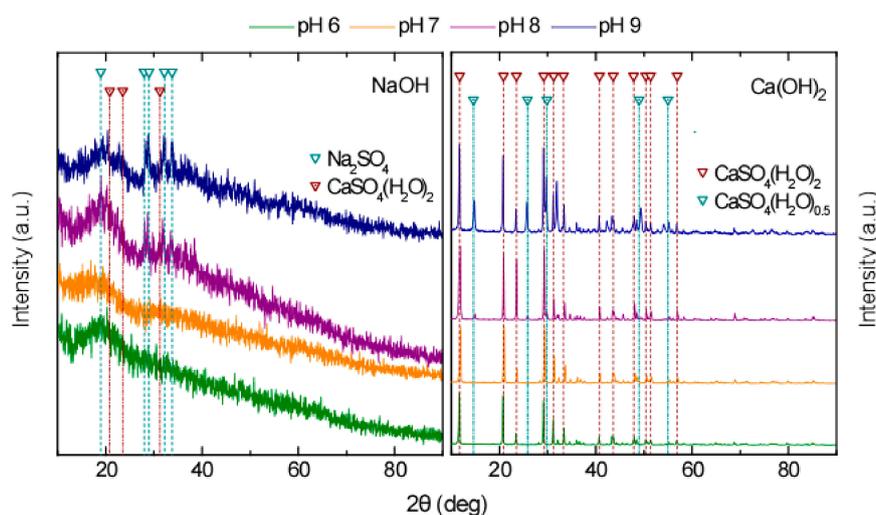


Figure 5. XRD spectra of the examined Cr precipitates by applying common alkaline reagents.

4. Conclusions

Hydrometallurgy proved to be a suitable methodology for the recovery of Cr(III) from tannery sludge, produced from the respective tanning wastewater treatment. The acid with the highest recovery efficiency was H_2SO_4 (93% for 1 N acid) as it forms more soluble salts, such as CrSO_4^+ species, than the other examined inorganic acids. The application of H_2SO_4 was also highly selective because it favored the formation of sparkly insoluble by-product CaSO_4 precipitate, resulting in a substantially lower dissolved calcium content in the produced leachate, hence limiting the co-precipitation with chromium. The effect of major experimental parameters showed that a further increase in chromium recovery can

be obtained by the application of a (moderate) increase in temperature, regarding both efficiency and selectivity. The increase in L/S ratio, although able to result in the even greater increase in efficiency of this process (recovery of chromium), is not suggested, because of the respective reduction in selectivity, as well as due to the use of larger acid volumes. Therefore, the following optimal recovery conditions of Cr(III) were defined: Acid concentration 0.5–1 N, temperature 40° C, contact time 60 min, and L/S ratio equal to 25. Among the examined alkaline media, NaOH yielded a precipitate containing up to 70% Cr(OH)₃, with the corresponding optimum pH value being at 8. By contrast, the use of Ca(OH)₂ showed a corresponding content of only 14% Cr(OH)₃ as, in this case, the formation of CaSO₄ was favored (up to 63%), highly reducing the purity of the precipitate with respect to Cr(III) content. Overall, it was revealed that the application of hydrometallurgy can provide a chromium-rich solid, which makes it easily manageable, e.g., during transfer, and it can also be appropriately reused in tanneries as a Cr(III) reagent.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/12/3/719/s1>, Figure S1: Speciation forms of Cr(III) using H₂SO₄ as leaching agent and applying the equilibrium data of this study, according to software Visual MINTEQ version 3.1. Figure S2: Speciation forms of Cr(III) using HNO₃ as leaching agent and applying the equilibrium data of this study, according to software Visual MINTEQ version 3.1. Figure S3: Speciation forms of Cr(III) using HCl as leaching agent and applying the equilibrium data of this study, according to software Visual MINTEQ version 3.1.

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

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