Article

The Most Used Methods of Chrome Extraction from Leather Polymer Wastes

Ana-Maria Nicoleta Codreanu (Manea) , Daniela Simina Stefan * , Lidia Kim , Mircea Stefan *

Posted Date: 12 May 2024

doi: 10.20944/preprints202405.0731.v1

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Review

The Most Used Methods of Chrome Extraction from Leather Polymer Wastes

Ana-Maria Nicoleta Codreanu (Manea) [1,2], Daniela Simina Stefan [3,*], Lidia Kim [2] and Mircea Stefan [4,*]

[1] PhD student, Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology Politehnica Bucharest, Romania, e-mail: anamaria.codreanu@ecoind.com
[2] National Research and Development Institute for Industrial Ecology, Department for Evaluation, Monitoring Environmental Pollution, Drumul Podu Dambovitei Street, No 57-73, ZIP Code 060652, Bucharest, Romania; lidia.kim@incdecoind.ro
[3] Prof. Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology Politehnica Bucharest, Department of Analytical Chemistry and Environmental Engineering, Polizu Street, No 1-7, ZIP Code 011061 Bucharest, Romania; daniela.stefan@upb.ro
[4] Associate professor "Titu Maiorescu"University, Pharmacy Faculty, 22 Dâmbovnicului Street, 040441, Bucharest-4, Romania, stefan.mircea@incas.ro
* Correspondence: daniela.stefan@upb.ro and stefan.mircea@incas.ro

Abstract: The leather industry is one of the most polluting industries in the world due to the large amounts of waste following the raw hides processing, but also due to the high content of chemicals present in their composition. The main problem of chromium-tanned leather solid waste is related to their storage, because of the ability of chromium to leach in soil or water, and also owing to the high ability of trivalent chromium to oxidize to its toxic form, hexavalent chromium. The purpose of this study is to present the latest methods for extracting trivalent chromium from the composition of solid leather wastes. The extraction methods identified in the present study are based on acid/basic/enzymatic hydrolysis and substitution with the help of organic chelators (organic acids and organic acid salts). In addition, the study includes a comparative analysis between the advantages and disadvantages of each identified extraction method. At the same time, the study also presentes alternative chromium extraction methods based on the combination of conventional extraction methods and ultrasound-assisted extraction.

Keywords: leather solid waste; chromium removal; hydrolysis method; substitution method; circular economy

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1. Introduction

Nowadays, industrial pollution is one of the biggest challenges all over the world. Leather industry is one of the most important industries from the world [1] and, in the same time, leather industry is known as one of the major polluting industries [2], due to the large amount of chemicals used, large amounts of leather waste produced, and chemical compounds discharged into waste water [3,4].

Leather industry is based on leather manufacturing, which is one of the oldest activities in the history of mankind [2]. This industry uses animal skins and hides as raw material [2], coming especially from the meat industry [5], to obtain a variety of products, such as: belts, clothes, shoes, bags [6]. Annually, the leather industry consumes approximately 8-9 million tons of raw skin and hide [7].

Because raw animal skins and hides are microbiologically unstable, it is necessary to implement a stabilization stage [8,9]. The transformation of raw hides into finished leather involves three major stages: pre-tanning (soaking, liming, fleshing, reliming, deliming, bating, pickling), tanning and finishing stage (retanning, dyeing, and fat liquoring) [10]. Pre-tanning operations are responsible with cleaning hide and preparing it for the second stage [11,12]. The tanning stage is one of the most important stages of the leather processing because this process transform raw skins into non-putrescible products [13], protects the leather against moisture, heat and microbial degradation, offering as well better dyeing characteristics and softness [1,2,14]. In the tanning stage, chromic or vegetable compounds can be used [10]. Chromium tanning process is the most commonly used process, being used by over 90% of leather manufacturing companies [15,16]. In the chromium tanning process, chromium ions are crosslinking to the carboxylic groups by the collagen present in the leather [8]. Chromium (III) salts ($Cr(OH)(SO_4)$) are among the most used tanning agents [17], and in the same time, in one of the most important source of leather industry pollution, (due to)/ caused by the large amount of solid waste contaminated with the chromium produced (sludge and chromium-tanned leather waste), and the large volume of contaminated wastewater generated [17].

The resources used into leather industry and the products resulting from the leather processing are described in Figure 1 [18].

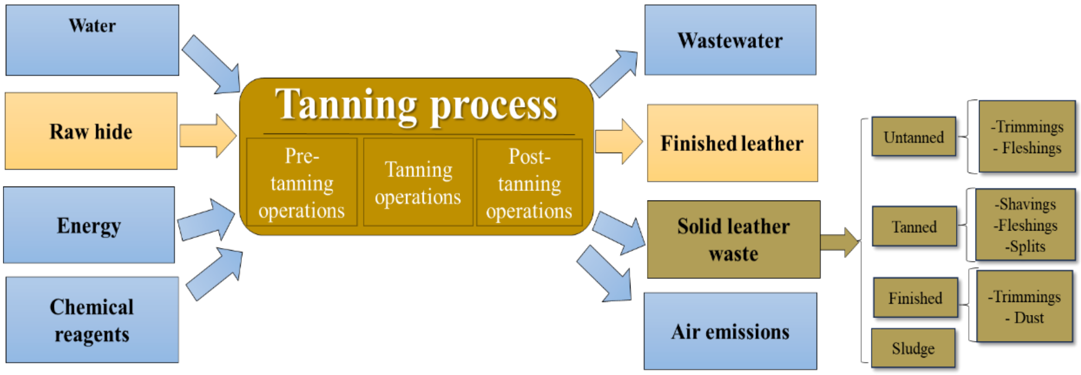

Figure 1. Tanning process: resources used, and waste generated.

As a consequence of raw hides processing, solid waste and wastewater are generated besides the final product. Leather solid waste is generated during the leather production process, by applying different mechanical steps that have the role of uniformity, and which standardize the dimensions of products. Leather solid waste can be classified as un-tanned solid leather waste (splits, flashings, and trimmings), and organic tanned waste (shavings, splits and trimming) [19]. During the manufacturing process of one metric ton of raw materials, the following elements are produced: 150-200 kg finished leather, 190-350 kg non-tanned waste, approximately 200-250 kg tanned waste, and the rest is composed of sludge and waste water [11,13,20,21].

Also, waste from leather processing operations is classified and presented in the European Waste Catalog (CED) as follows [22]:

04 WASTES FROM THE LEATHER, FUR AND TEXTILE INDUSTRIES
04 01 wastes from the leather and fur industry
04 01 01 fleshing's and lime split wastes
04 01 02 liming waste
04 01 03* degreasing wastes containing solvents without a liquid phase.
04 01 04 tanning liquor containing chromium.
04 01 05 tanning liquor free of chromium
04 01 06 sludges, in particular from on-site effluent treatment containing chromium.
04 01 07 sludges, in particular from on-site effluent treatment free of chromium
04 01 08 waste tanned leather (blue sheetings, shavings, cuttings, buffing dust) containing chromium.
04 01 09 wastes from dressing and finishing
04 01 99 wastes not otherwise specified.

The influence of the tannery process on the environment can be monitored by analyzing some parameters, such as: total dissolved solids (TDS), chemical oxygen demand (COD), sulphates, chlorides, and heavy metals pollution [23].

Managing the large quantities of solid leather waste produced is a challenge for this industrial sector. The conventional methods of managing solid leather waste are disposal and incineration. Even if these methods are simple and inexpensive, they can be applied just for un-tanned solid waste, while for chromium tanned leather waste, conventional methods are not practicable, because they produce soil, water and air contamination due to the hazardous reagents present in their composition. Chromium tanned lather waste incineration can generate the conversion of Cr^{3+} to Cr^{6+}, nitrogen oxides, ammonia emissions, and hydrogen cyanide [8,19,24]. Also, the storage of solid waste from chromium-tanned leather presents the leaching problem of the chromium into the soil and underground water, and it can oxidize to toxic form Cr^{6+}, affecting the health of the environment and human health. Thus, the main problem regarding the management of chromium-based solid leather waste is given by the presence of chromium in their composition.

Chromium is an essential micro-nutrient in human and animal diet, and/ being in the same time, a toxic metal for plants and microorganisms [25]. This metal can exist in different oxidation states (Cr^{2+} to Cr^{6+}), but in soil it is mostly found in two oxidation states: hexavalent chromium and trivalent chromium [26]. Chromate is the most widespread form of hexavalent chromium, and the most mobile chromium forms in soil [27]. Chromium presence in the two oxidation states shows different chemical and physical characteristics, and as well as opposite toxicities: Trivalent chromium presents low toxicity, while hexavalent chromium presents high toxicity [28]. Trivalent chromium toxicity is from 10 to 100 times less than the hexavalent chromium toxicity [27]. The oxidation of trivalent chromium to hexavalent chromium is pH dependent. The possible oxidation process is described by the following equations [29]:

$$2Cr_2O_3 + 8OH^- + 3O_2 = 4CrO_4^- + 4H_2O$$

$$2Cr_2O_3 + 2H_2O + 3O_2 = 4Cr_2O_7^- + 4H^+$$

In 2022, hexavalent chromium is included on the list of the Substance Priority List issued by The Agency for toxic Substances and Disease Registry, being in the top 15 [30]. Even in small doses, hexavalent chromium affects human health, causing respiratory problems, cancer, skin ulcers and allergic reactions [15,31], and ingested in a small dose, it causes human and animal death [32]. A large part of solid and liquid chromium-based waste comes from the leather industry, the mining industry, the dyes and pigments industry, and the textile industry [27]. Even if the chromium salts used in the leather processing process do not contain hexavalent chromium, chromium solid leather waste contain hexavalent chromium, d because of the dyeing additives, pigments, and fixing agents used in finishing stages, or due to non-compliance with optimal manufacturing or storage conditions.

Owing to the useful components present in the composition of solid tanned leather waste, alternative methods of managing thousands of tons of chromium solid leather waste are based on thermal decomposition (pyrolysis), microbial enzymatic degradation (aerobic degradation, anaerobic degradation, bioremediation), and obtaining of value-added products [33]. Because chrome-tanned leather shavings contain approximately 90% collagen protein and between 3-6% chromium [34,35], which are valuable products, these can be reused in various fields by applying the circular economy principle (Figure 2) [36].

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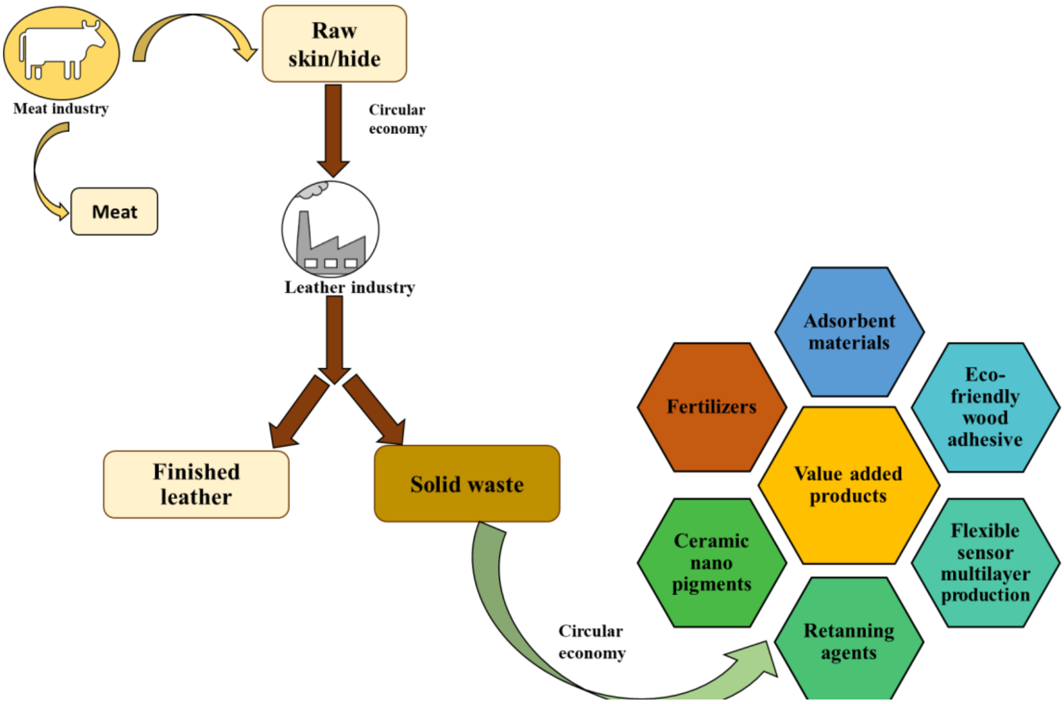

Figure 2. Valorization of solid leather waste by applying the circular economy principles.

For example, due to the high content of chromium, solid waste from tanned leather can be used to produce ceramic nano pigments [37,38], or to produce retanning agents in the leather industry. At the same time, due to the high content of carbon and nitrogen present in the protein part, solid waste from tanned leather can be used in the production of fertilizers [39], flexible sensor multilayer production [40], eco-friendly wood adhesive [41], biofuels , biochar [24,42], adsorbent materials [43,44], and construction materials [45,46].

2. Chromium Extraction Methods

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Interventionary studies involving animals or humans, and other studies that require ethical approval, must list the authority that provided approval and the corresponding ethical approval code.

The most common methods to significantly reduce the amounts of hexavalent chromium from waste, soils, sludges are based on precipitation, reduction, adsorption, ion exchange and reverse osmosis [27]. The tannery chromium (VI) contaminated soils can be treated using microbial reduction methos in presence of molasses, microbes, native bacteria [47,48].

The recovery of chromium (III) from chromium solid leather waste is justifiable from ecologically and economically point of view, because it reduces the risk of soil, water, air contamination. The extracted chromium can be reused, as well as the other valuable components such as collagen, lipids. The purpose of this article is to present the most current methods of chromium extraction from the composition of solid waste from tanned leather.

Chromium tanned leather waste is the result of a covalent bond between the chromium ion and ionized carboxyl groups, belonging to aspartic and glutamic acids present in the composition of collagen [49]. Chromium-chromium bonds and chromium-collagen bonds are broken during the dechroming process of solid tanned leather waste. Dechroming can be done by hydrolysis, and by the substitution method. The most used dechroming methods are hydrolysis (acid/basic/enzymatic) and substitution method, with the help of/ by means of organic chelators [50].

Figure 3 presents the most used chromium extraction methods from chromium tanned leather waste. Dechroming by hydrolysis is one of the most practiced dechroming methods and can be acidic, alkaline or enzymatic. The hydrolysis method is based on the dissociation of functional groups from the Cr-collagen matrix. Acid and alkaline hydrolysis have one thing in common: the protein obtained (by them) presents low molecular weight [51]. After the hydrolysis process, a protein part (peptides or amino acids) and chromium cake can be obtained, these being valuable compounds that can be reused [52].

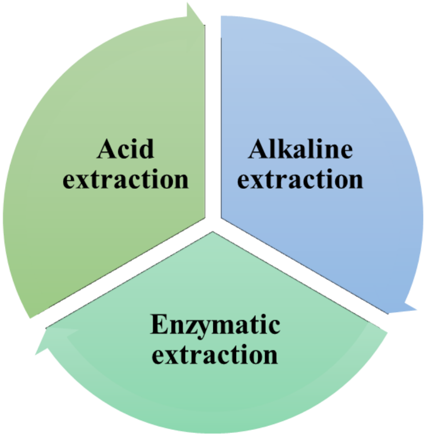

Figure 3. The most used chromium extraction methods from chromium tanned leather waste.

Depending on the hydrolysis method applied, the protein part (collagen) can be slightly denatured or strongly denatured, and it can be used in various fields, depending on the degree of hydrolysis [36]. Also, collagen extracted from animal hides of from leather waste is one of the main renewable natural resources. In animals hides and skins, the most predominant type of collagen of the 29 types is type I collagen [53]. Type I collagen is a water insoluble protein, having a triple helix structure and therefore present great industrial interest [54]. Gelatin is obtained from partial denaturation of collagen. This important biopolymer can be extracted from solid waste leather using alkaline, acid or a combination alkaline-acid treatment, followed by thermal hydrolysis. The obtained gelatin can be of 2 types: type A gelatin (obtained in acidic conditions) and type B gelatin (obtained in alkaline conditions) [55]. The hydrolysis process weakens the collagen structure, dissolve non-collagen protein, partially hydrolyze the peptide bond and kill bacteria. Gelatin from chromium tanned solid leather has an excellent gel formation capacity, high biodegradability and low costs. (In Table 1 was showed) The optimal extraction conditions of chromium from chrome-tanned solid waste are showed in Table 1.

Table 1. Optimal extraction conditions of chromium from chrome-tanned solid waste.

Chromium removal method	Chromium removal method	Chromium extraction yield	The degree of collagen hydrolysis	Reference
Acid extraction	-Concentration of extraction solution = 8%	>95%	-*	[56]

	H_2SO_4 -L-S ratio = 11:1 -Time= 2.5 hours -Temperature= 343 K			
Acid extraction	-Concentration of extraction solution= 25 mL/L H_2SO_4 -Time= 3 or 6 days	30%-60%±5%	3-6±1%	[57]
Acid extraction	-Sample amount= 150 mg -Concentration of extraction solution= 3 mol/L HNO_3 -Temperature= 30℃ -Time= 30 minutes	92%	-	[58]
Acid extraction	-$H_2C_2O_4$: H_2SO_4: sample ratio= 2:1:1 -Time= 12 h -Processing times= 1 hour -Stirring speed= 250 r/min -Temperature= 40 °C	95.6%	90.6%	[59]
Acid extraction	-Extraction agent: oxalic acid -Time= 36 hours -Room temperature -pH= 5,5 -Cr-oxalic acid ratio= 1:3	71%	-	[60]
Acid extraction	-Concentration of potassium tartrate= 0.5 M -NaOH solution concentration= 0.25 M -Room temperature -Time= 72 hours	95%	-	[61]
Acid extraction	-Concentration of sodium oxalate= 2% -L-S ratio= 200 mL/g -Thickness of sample= 0.5 mm -Temperature= 333 K -Time= 5 hours -Stirring speed= 150 rpm	98%	>95%	[62]
Acid extraction	-Sample amount= 3 g -Cr^{3+} : EDTA ratio= 1:3 -Temperature= 80℃ -Time= 30 de minutes -5 washing cycles with water (V=50 mL), at a temperature of 50℃, for 3 minutes each	98%	-	[63]
Acid extraction	-EDTA: Cr^{3+} ratio= 3:1 -US power= 150 W -Frequency= 20 KHz -Residence time= 60 minutes -Temperature= 70 °C	71.7%	-	[64]
Alkaline extraction	-Concentration of extraction solution= 0.2 M NaOH -L-S ratio= 80 cm^3/g -Time= 1 hour -Temperature= 60 °C	90%	~ 100%	[65]
Alkaline extraction	-Concentration of extraction solution= 0.47M NaOH -Time= 90 minutes	750.8 g	87.165%	[66]

	-Temperature= 70 ° C			
Alkaline extraction	-Concentration of extraction solution= 3% NaOH -Time= 180 minutes -Temperature= 90 °C -L-S ratio= 5:1	~100%	-	[67]
Alkaline extraction	-Concentration of extraction solution= 4 M NaOH -S-L ratio= 0,15 -Time= 90 minutes -Temperature= 423 K	85%	98%	[68]
Alkaline extraction	-H_2SO_4 concentration= 0.1 N H_2SO_4 -Dose of Gamma radiation ^{60}Co= 60 Krad -Concentration of extraction solution= 1 N NaOH	~100%	25%-40%	[69]
Alkaline extraction	-Concentration of extraction solution 1= 2 g/L NaOH, stirring for 30 minutes at 30 °C, urea concentration= 40 g/L -Concentration of extraction solution 2= 50 g/L H_2SO_4, stirring for 1 hour at 30 °C -Concentration of extraction solution 3= 40 g/L CaOH, stirring for 2 ore at 30 °C -Concentration of extraction solution 4= 50 g/L H_2SO_4, stirring for 1 hour at 30 °C	97%	10%	[70]
Enzymatic extraction	-Extraction solution concentration= 6% MgO -Bating enzyme concentration= 0.75% -Time= 30 hours -Temperature= 33-37 °C -pH= 8.3-8.5	99.99%	-	[71]
Enzymatic extraction	-Extraction solution MgO -Stirring speed= 60 rpm -Temperature= 70 °C -Time= 6 hours -*Bacillus subtilis enzyme A proteolitic* activity= 130.5 U/mL -pH= 9 -Time= 15 hours -Temperature= 45 ° C -Stirring speed= 60 rpm	~100%	-	[72]
Enzymatic extraction	-Extraction solution concentration= 3% MgO -Extraction solution concentration= 3% CaO -Temperature= 80 °C -Time= 4 hours -1398 neutral protease concentration= 0.125% -Temperature= 46 °C	~100%	>60%	[73]

3. Acid Extraction of Chromium

Acid methods used inorganic acids (sulphuric acid, hydrochloric acid, and azotic acid) and organic acids (oxalic acid, citric acid, tartric acid) for dechroming of chrome-tanned solid waste [59]. Figure 4 presents the main classes of acids used to extract chromium from chromium tanned solid wastes.

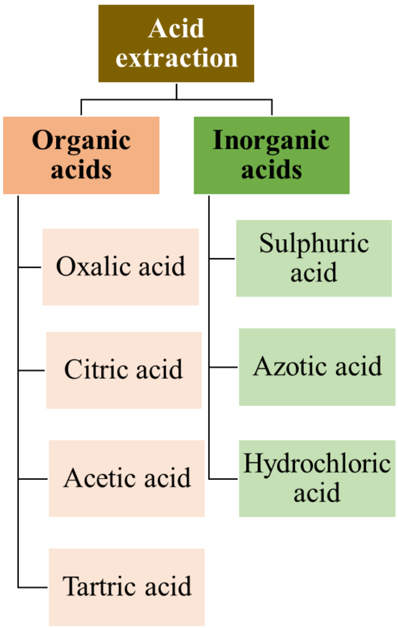

Figure 4. The main classes of acids used to extract chromium from chromium tanned solid wastes.

In this method, the chromium combines with the strong acid groups and thus, it is obtained a soluble complex that can be extracted from the solution [56]. Conventionally, oxalic acid has been the best acid reagent for dechroming, followed by sulfuric acid, but the large-scale use of organic acids in the treatment of tanned leather solids is limited, because of the high prices. Consequently, sulfuric acid became the first choice of many researchers, being used in numerous studies as a dechroming agent for tanned leather [56]. The main advantage of acid methos is the possibility of reuse acid solution containing chromium in leather industry in tanning, pickling and dyeing stages [59].

In acid hydrolysis, inorganic acids H^+ can replace trivalent chromium ions, and is combined with COO^- of collagen. The advantages of dechroming using the acid method are stable products, low cost, easy control and implementation [59].

The dechroming process of chromium tanned leather sample using sulphuric acid at low temperature was studied by varying some indicators such as: sample dimensions, temperature, extraction time, sulphuric acid concentration, and sodium sulphate concentration [57]. By increasing the concentration of sulfuric acid from 35 mL/L to 200 mL/L, an improvement in chromium extraction performance could be observed, but a high concentration of sulfuric acid leads to matrix degradation. The temperature has also a similar influence on the extraction process, by changing the temperature from 296 K to 313 K, the chrome recovery yield improves, but the degradation of the protein matrix takes place. The variation in the size of the leather waste (4 mm or at sizes of 5 cm*3 cm) did not significantly influence the chromium extraction process, the same insignificant influence being also observed in the case of the variation of the L-S ratio (from 5:1 to 10:1). The research team proposed two optimal chromium extraction formulas. If it is desired to obtain a high chrome recovery yield (55-60±5%), but with a high degree of denaturation of the tanned leather (dissolved TOC is 3-6%), the leather waste can be subjected to solution treatment of H_2SO_4 25 mL/L, in a L-S ratio between 5:1 or 10:1, for 3-6 days at 313 K. If a moderate chromium recovery yield is desired (35±5%), but with a low degree of denaturation of tanned leather (TOC <3-6%), the leather waste can be treated with 25 mL/L H_2SO_4 solution, in a L-S ratio between 5:1 or 10:1, for 6 days at 296 K [57].

In addition, Wang and co. studied the complete removal of chromium from chromium leather waste in two steps, using the acid extraction chromium method and ion exchange step, for removing the chromium found in the composition of the filtrate with the help of ion exchange resins. By varying some parameters involved in the extraction process, such as: the liquid-solid ratio, sulfuric acid concentration, contact time and reaction temperature, they could observe that the factor that most strongly influences the extraction yield is the reaction temperature (50°C-70°C), followed by the sulfuric acid concentration (6%-10%), the liquid-solid ratio (9:1 mL/ g to 11:1 mL/g), and finally, by the reaction time (2.5 hours to 3.5 hours). By setting the liquid-solid ratio at 11:1 mL/g, the sulfuric acid concentration at 8%, the contact time at 2.5 hours, and the reaction temperature at 70°C, an efficient removal of chromium from leather waste was obtained, close to 100% [56].

However, conventional acid/base/enzymatic hydrolysis can break the peptide bond in collagen, thus resulting in destroyed collagen, which can be difficult to be removed from the hydrolysate. Chromium extraction from chromium-tanned leather waste by means of organic acids or their salts has the advantage of efficiently removing chromium, without significantly degrading the collagen matrix.

Dechroming using organic acids/salts is based on organic acid anions coordination with trivalent chromium using the substitution method. The dechroming process presents two stages. In the first stage, the breaking of the chromium-collagen bonds present in the composition of solid waste from tanned leather takes place through the substitution reaction (exchange) of a water molecule around the first chromium atom with the ionized carboxylic group belonging to the organic chelator, followed by the breaking of the first bond chromium-collagen, to restore the coordination amount of chromium. In the second stage, the ionized carboxylic groups of the organic chelator attack the second chromium atom, followed by the breaking of Cr-collagen bonds, to restore the coordination number [61]. The main advantages of this method are low hydrolysis degree of collagen, high collagen recovery yields, and low amounts of dangerous materials generated [59]. In the same time, the loss of collagen from chrome-tanned solid waste using organic acid extraction is lower than alkaline method [59].

The efficiency of chromium separation from chromium leather waste using organic acids (acetic acid and citric acid) and organic salts (potassium oxalate and potassium tartrate) was tested by Malek and co [61]. The experimental results demonstrated a direct influence of some parameters involved in the process, such as: the type of chelating agent used, the type of extraction medium, the concentration of the chelating agent, the concentration of the extraction medium, the temperature and the contact time on the chromium extraction yield (III). The tests regarding the choice of the organic chelator carried out in the neutral environment demonstrated the fact that the salts of organic acids have a higher capacity to extract chromium, compared to the organic acids used in the extraction processes. This fact is due to the presence of the alkaline environment in the case of salts, which can form stronger bonds between the carboxylic groups and chromium more easily, while the acidic environment can inhibit the reaction. Also, by testing the medium suitable for the extraction process, it was possible to conclude that, for all four organic chelating agents, the highest extraction yields are obtained in the basic medium (94.3% when potassium tartrate is used in the basic medium). By studying the effect of the potassium tartrate concentration on the extraction yield, it was observed that, by increasing the concentration of the chelating agent (0.005 M, 0025 M, 0.05 M, 0.25 M, 0.5 M, 1 M) the pH values also increase. The stabilization of the pH leads to a significant increase in the extraction yield, thus the optimal value of the potassium tartrate concentration was 0.5 M. Also, by progressively increasing the concentration of the alkaline solution (0.01M, 0.05M, 0.1 M, 0.25 M, 0.5 M, 1 M), the pH tends to be increasing, and the Cr removal efficiency tends to follow the same trend. A concentration higher than 0.5 M leads to the degradation of the sample matrix, due to the strong manifestation of the phenomenon of hydrolysis of hydroxyl groups on the chromium-collagen complex. Through the simultaneous study of the influence of temperature (25, 30 and 40°C) and contact time (30, 90 and 180 minutes), the results obtained showed that temperature and reaction time have significant effects on the efficiency of chromium extraction. A decrease in the residual chromium concentration could be observed by keeping the temperature constant at 40 °C and varying the contact time.

Also, the extraction efficiency of chromium (III) from the composition of solid waste from tanned leather with the help of organic acid salts (sodium gluconate, trisodium citrate, EDTA-2Na, sodium oxalate, sodium, and potassium tartrate) was also studied [62]. The type of chelating agent studies demonstrated that that all organic chelators tested show good chromium extraction capabilities, due to the presence of carboxylic groups in their molecule, which show a strong ability to complex chromium. The chromium extraction efficiency decreases with increasing the chelating agent molecule size and with the increase of carboxylic groups number. The most suitable chelating agent was sodium oxalate. he existence of a directly proportional relationship between the extraction yield and the sodium oxalate concentration (1-3%) was observed. The optimal value of sodium oxalate concentration was 2%, because after this value the phenomenon of denaturation of the collagen matrix appears. Also, the extraction yield of chromium is significantly influenced by the increase in temperature (318 K-338 K), and it increases with the increase in temperature, the optimal temperature being of 333 K, because above this temperature, the collagen matrix is destroyed. Further studies on the influence of the thickness of tanned leather waste samples (0.5 mm-2.3 mm), and the stirring speed (0 to 150 rpm) - demonstrated that decreasing the thickness of the waste improves the extraction yield, and increasing the speed of stirring also leads to a significant improvement of the extraction yield [62].

In addition, the influence of heteroatomic organic compounds (8-hydroxyquinoline, acetylacetone, dithizone, thiourea DMSO), and the influence of organic compounds containing the carboxyl group in the molecule (maleic acid, citric acid, oxalic acid, tartaric acid, salicylic acid, EDTA) on the dechroming process of tanned leather solid waste was studied [60]. The experimental results demonstrated that the most effective chelating agents are those containing the carboxyl group in the molecule, and the best chromium extraction yield from these wastes was obtained for oxalic acid (71%), followed by citric acid (63%), and tartaric acid (62%), the extractions being carried out in a single step. In contrast, the compounds containing sulfur atoms in the molecule (dithizone, thiourea, DMSO) showed the weakest results (0%-3%). Studies on the influence of pH, temperature and contact time on the extraction efficiency of oxalic acid and citric acid was demonstrated that an increase in pH towards the neutral medium significantly improves the extraction yield for both acids, and using the higher temperatures significantly decreased the extraction time and the chromium extraction yield was increased. At temperatures exceeding 60 °C, the protein matrix in the analyzed waste was destroyed.

Considering the advantages and disadvantages of the two methods of extraction in acidic environment (extraction with inorganic acids, and extraction with organic acids), the team coordinated by Tian studied the extraction of chromium by applying a combined acid extraction method, using a mix between an organic acid (oxalic acid) and an inorganic acid (sulfuric acid). The studies carried out followed the influence of the mass ratio between oxalic acid: sulfuric acid: tanned leather waste, but also the influence of the time interval at which the acid solution is refreshed on the chrome extraction yield, and on the collagen recovery yield. By varying the mass ratio of oxalic acid: sulfuric acid: leather waste in the range 1:0.5:1-3:1.5:1, it was possible to observe that the optimal ratio is 2:1:1, by obtaining a degree of dechroming of approximately 96.5 %, and a collagen recovery yield of 90.6%. Also, by varying the time interval in which the acid solution is refreshed, it was found that the best collagen recovery yield and the best degree of dechroming over 90% are obtained, then the solution changes 3 times in 12 hours. The main advantages of the developed method were based on obtaining a collagen with high molecular weight, high yield of chromium extraction and moderate costs [59].

4. Alkaline Extraction of Chromium

Alkaline hydrolyses can be done using calcium oxide, magnesium oxide, sodium hydroxide, potassium hydroxide, and calcium hydroxide. In alkaline hydrolysis, the coordination of the chromium ion (III) to the hydroxide ion takes place, and the precipitation of trivalent chromium in $Cr(OH)_3$ can be observed, while the collagen is hydrolyzed and dissolved. Cr^{3+} formed from the soluble hydroxy complex can later be separated by extraction with another solvent (for example quaternary ammonium compounds) [65]. Figure 5 presents the advantages and disadvantages of alkaline extraction of chromium [59].

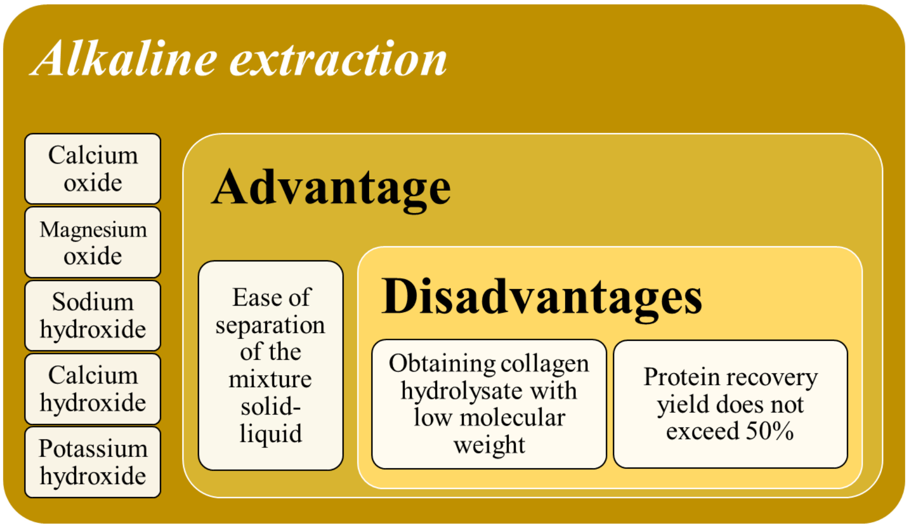

Figure 5. The main advantages and disadvantages of alkaline extraction of chromium from chromium tanned solid wastes.

The study of the influence of the sodium hydroxide concentration, contact time and temperature on the chromium (III) extraction process from the composition of tanned leather waste through the basic hydrolysis process was carried out by Wionczyk and co [65]. The experimental results demonstrated that the extraction yield of chromium from the chromium-collagen matrix can be improved by increasing the concentration of sodium hydroxide from 0.2 M to 0.3, increasing the degree of hydrolysis of the protein matrix at the same time. By increasing the temperature in the range of 313K-343K, it could be observed that a high chromium extraction yield is reached in a shorter time. Under optimal conditions of 60°C, one hour contact time, and 0.2M NaOH concentration, chromium (III) was efficiently separated from the collagen-protein matrix, the extraction yield reaching the value of 90%. However, following the application of the optimal extraction conditions, the collagen present in the solid waste from the skin was completely hydrolyzed, this aspect constituting a serious disadvantage [65].

Studies on the influence of the hydrolysis time (1-3 hours) and the concentration of the extraction agent (1%-3% NaOH) at a temperature of 90 °C on the results of the basic hydrolysis process of leather shavings scrap were also carried out by Pahlawan et al [67]. The experimental results demonstrated that, by increasing the contact time to 3 hours and the NaOH concentration to 3%, a hydrolysate with a protein content of 6.64% and a chromium content of 47.55 ppm are obtained (the initial chromium content in leather shavings scrap being 23176.14 ppm) [67]. The same studies regarding the influence of the hydrolysis time, as well as the concentration of sodium hydroxide on the chromium extraction process from chrome shavings, were also carried out by the research team led by Tahiri [74]. The optimal conditions were 15 minutes of reaction time, and 0.5M solution concentration of sodium hydroxide [74].

The alkaline extraction of chromium from chrome leather shavings with the help of sodium hydroxide was also studied by Barra Hinojosa and collaborators [66]. In the study, the relationship between working conditions (contact time and sodium hydroxide concentration) and the recovery yield of hydrolyzed collagen, and chromium recovery yield, respectively, was studied. It was found that by increasing the concentration of sodium hydroxide (0.1 M-0.5 M), the hydrolysis reaction is improved, the optimal concentration being of 0.47 M. By varying the contact time between 30 minutes and 120 minutes, it was found that, increasing the contact time, the separation of chromium from the chromium-collagen matrix is improved, the optimal contact time being of 90 minutes. Thus, in optimal condition (70 °C, 0.47 M NaOH, 90 minutes) 45 L of collagen hydrolysate with 87.16% protein collagen, and 1.17% residual chromium were recovered [66].

Also, the research team of Ferreira et al studied the chromium extraction efficiency from solid salts using sodium hydroxide as the extraction medium, and also temperature, contact time, and S-L ratio effect [68]. Studies of the influence of the sodium hydroxide solution concentration (0 M-4 M) demonstrated that the NaOH concentration is one of the most important factors of chromium extraction process. By increasing the NaOH concentration, as in the case of the study carried out by Wionczyk, an increase in the chromium extraction yield was observed, as well as a significant degradation of the collagen matrix. At the same time, studies have shown that temperature (373 K-473K) and contact time (1-24 hours) are important factors. Their increase leads to significant degradation of the collagen matrix (almost completely). In contrast, the S-L ratio has no significant effect on the chromium (III) extraction yield [68]. The more suitable conditions were: temperature of 423 K for 1.5 h with NaOH 4 mol/L solution, and solid to liquid (S/L) ratio (w/w) of 0.15 or 0.2.

In order to reduce the disadvantage of the destruction of the collagen matrix during the extraction of chromium process from tanned leather waste, the research team led by Poulopoulou implemented two additional steps to protect the protein matrix with H_2SO_4 and Gamma radiation, in addition to the extraction step with NaOH [69]. Also, the research carried out in the study demonstrated that the introduction of a final extraction step with hydrogen peroxide leads to the improvement of the chromium extraction yield, with the final amount of chromium in the tanned leather solid waste being below 10 ppm. The study of the influence of the concentration of sulfuric acid demonstrated that the increase in the concentration of sulfuric acid (0.1 N-1 N) directly proportionally influences the degree of denaturation of the protein, as well as the chromium extraction yield, while the study of the influence of the Gamma radiation dose demonstrated that an increase in this parameter leads to an increase in the denaturation of the protein matrix. Concentration of NaOH higher than 1N leads to the destruction of the protein part, and a concentration below this value significantly reduces the chromium extraction yield [69].

At the same time, to improve the dechroming yield, but also to keep a low degree of collagen hydrolysis, an alternating acid-base extraction process was tried on the solid waste from tanned leather [70]. Chromium extraction was carried out in four stages, as follows: basic extraction with NaOH; acid extraction with H_2SO_4; basic extraction with $Ca(OH)_2$; acid extraction with H_2SO_4. At the same time, to improve the results obtained in the study, the influence of hydrolysis assistants (ammonium hydroxide, diethanolamine, methyl-urea, guanidine hydrochloride and urea), reaction temperature, sulfuric acid concentration, and calcium hydroxide concentration were studied. It could be observed that all the compounds with amino groups used as hydrolysis assistants are able to increase the degree of dechroming, urea having the best capacity (65.66%). It could be observed that the largest amounts of chromium were extracted in the first two stages. By varying the concentration of $Ca(OH)_2$, it was possible to observe that a high degree of chromium extraction is obtained at the optimal concentration of 40 g/L, below this value the degree of collagen hydrolysis being lower. It has been reported that Ca^{2+} has a compressive effect on collagen fibrils at high concentration, and thereby protects the collagen fibrils from excessive damage [70].

5. Enzymatic Extraction of Chromium

Enzymatic extraction of chromium is based on hydrolysis of collagen, and chromium release in the same time [59].The advantages and the disadvantages of this method are presented in Figure 6 [59].

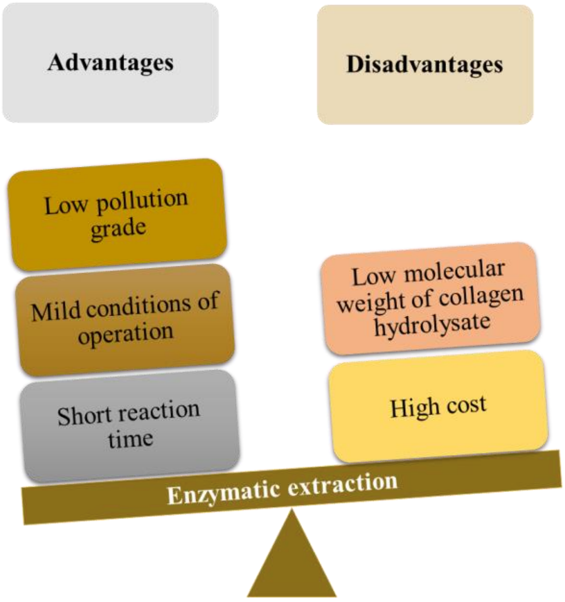

Figure 6. The main advantages and disadvantages of enzyme extraction of chromium from chromium tanned solid wastes.

The molecular weight of the collagen hydrolysate can be influenced by the reaction mixture and concentration of enzymes. Also, the economy of the process can be influenced by a whole series of factors, such as: enzyme price, enzyme concentration, reaction speed, reaction time, reaction yield [75].

Due to the limitation given by the recovery of the protein part from the obtained hydrolysate and the chromium recovery, the combination of two types of hydrolysis was tried. Enzymatic hydrolysis is performed in two steps: a chemical pre-treatment step, followed by the enzyme addition step. A pre-treatment step is mandatory in enzymatic hydrolysis because gelatin produced after the first step helps to obtain hydrolyzed collagen in the second stage, by means of enzymes [52].

For example, alkali-enzymes hydrolysis is composed of two stages: in the first stage basic hydrolysis takes place (with the help of NaOH, CaO, MgO), and the second stage, in which enzymatic hydrolysis is applied to the residue left from the previous stage.

Asava and the collaborators tried to apply a combined alkali-enzymes hydrolysis process, to recover the chrome, and to improve the recovery efficiency of the protein part from chrome shavings tannery. They applied a stage of pre-treatment of the waste with MgO to denature, degrade and to increase the vulnerability of the collagen to the proteolytic attack, which followed in the next stage with the help of bating enzymes. After the first stage of basic hydrolysis with MgO 6%, the hydrolysis yield was 58.2% and the chromium content in the hydrolysate was 2.89 ppm (initial content was 3.04%). In the enzymatic hydrolysis stage, the effect of enzyme concentration (0.25-1%) and contact time (0-40 h) on protein recovery yield were studied. It could be observed that at the 0.75% enzyme concentration and 30 hours contact time, the total yield of protein recovery exceeded 79.45%, and chromium was extracted in a proportion of 99.99% [71].

The extraction of chromium and hydrolyzed collagen from solid chromium tanned waste combining two method (alkaline hydrolysis and enzymatic hydrolysis) was also studied by Dettmer and colleagues [72]. In the alkaline hydrolysis stage, they studied the influence of two extraction reagents (NaOH 0.1 M and MgO) on the efficiency of the chromium and collagen protein extraction process. The experimental results demonstrated that, in the same reaction conditions (stirring of 60 rpm, 70°C and 15 hours), a larger amount of protein is extracted by using MgO and 0.133 mg/l total chromium. In the enzymatic hydrolysis stage, the influence of two crude proteolytic enzymes: enzyme A (obtained by cultivating *Bacillus subtilis Blbc* 11), and enzyme B (obtained by cultivating *Bacillus subtilis Blbc* 17) on the of chromium extraction yield and the hydrolysate extraction yield from chromium cake obtained in the first stage was studied [72]. It can be observed that the liquid extracted from the hydrolysis carried out by the enzyme A, had lower chromium content (0.171 mg/L), while enzyme B had higher chromium content (0.359 mg/L) [72].

In addition, the use of two oxides mixes (CaO and MgO) in the alkaline hydrolysis step, followed by enzymatic hydrolysis with the help of 1398 neutral protease, to recover the hydrolyzed protein and chromium from chrome tanned pig leather shavings was suggested by Qiang et al. [73]. Studies on the influence of MgO: CaO alkali dosage (0:1, 2;3, 1:1, 3:2, 1:0), alkaline hydrolysis temperature (60-100°C,) alkaline reaction time (3-7 h), enzyme dosage (0.03-0.15%), and enzyme hydrolysis temperature (42-50°C) on the hydrolyzed protein extraction yield, and on the chromium extraction yield were achieved. The results showed that a hydrolyzed protein recovery yield of more than 60% is obtained when using the dosage of calcium oxide and magnesium oxide of 3%, alkaline hydrolysis temperature of 80°C, time 4 h, enzyme dosage 0.125%, and enzyme hydrolysis temperature of 46 °C, while the chromium content in the final hydrolysate after desalination was less than 50 mg/Kg [73].

Moreover, the research team led by Rahaman, carried out parallel studies regarding the influence of acid hydrolysis, the influence of acid-alkaline hydrolysis, and the influence of acid-alkaline-enzymatic hydrolysis on the chrome extraction yield from chrome shaving dust [76]. In the studies on acid hydrolysis, the influence of the type of acid extraction agent (H_2SO_4, HNO_3, HCl) and their concentrations (1M-6M) was studied. Experimental studies demonstrated that HNO_3 6M has the best chromium recovery capacity (70.09%). The studies on acid-alkaline hydrolysis with the help of CaO, MgO, NaOH, and the acids H_2SO_4, HNO_3, HCl, demonstrated that all the 3 alkaline media have nearly the same ability to recover chromium, but the mixture of MgO and HNO_3 presents the best extraction capacity of chromium (43.71%). Following the studies on acid-alkaline-enzymatic hydrolysis carried out with the help of the 3 acids, the 3 bases listed previously, and with the help of proteolytic enzyme, it was concluded that this technique significantly improves the chromium extraction yield. The best chromium extraction yield was 55.51% when MgO, NHO_3 and proteolytic enzymes were used.

6. Ultrasound Assisted Extraction of Chromium

Chromium extraction processes that are based on enzymatic treatment or alkaline-acid treatments are strongly affected by the formation of metabolic inhibitory products, and by the high costs of purchasing pure enzymes − in the case of enzymatic hydrolysis, respectively by the use of concentrated reagents, numerous steps and a relatively long reaction time (72 h) − in the case of acid-alkaline treatments. In addition, both processes lead to significant degradation of the protein matrix in the hide waste, reducing the quality of the raw material. Considering the disadvantages listed above, ultrasound-assisted extraction of chromium can be a sustainable alternative to existing methods of extraction of chromium from leather waste. Studies have shown that the additional application of ultrasound in the chromium extraction process from solid tanned leather waste significantly improves the chrome extraction yield from this waste, due to the effects caused by acoustic cavitation [63].

Ultrasound propagation process involves cavitation bubbles, vibrations, crushing, mixings and other comprehensive effects in the liquid medium [77]. When ultrasound is applied in extraction processes in a liquid medium containing solids, in the liquid−solid interface, bubbles can be formed with further collapse (cavitation), increasing the surface area of the substrate, as well as the transport rates of extraction solution [78]. Among the main advantages of ultrasound-assisted extraction there are: the short extraction time, but also the use of mild extraction conditions (temperature, concentration and amounts of reagents) [79].

The results of the study carried out by Bizzi and colleagues highlighted the fact that, by the additional application of an ultrasonic stage in the chromium extraction process in acidic medium (HCl, NHO_3, H_2SO_4, CH_2O_2, $C_2H_2O_4$), the chromium extraction yield is significantly improved [58]. Studies revealed that ultrasound-assisted extraction leads to a chromium extraction yield of 92%, while the application of the agitation step leads to a chromium extraction yield of 65%. Also, the studies related to the influence of some operating parameters such as: the type of extraction solution, the concentration of the extraction agent, the temperature, the time, the amount of the sample and the amplitude, demonstrated the existence of a direct relationship between the extraction yield of chromium (III) and these parameters. By testing 5 inorganic acids used as chromium extraction medium (HCl, NHO_3, H_2SO_4, CH_2O_2, $C_2H_2O_4$), it was revealed that nitric acid has the highest chromium extraction capacity, owing to its oxidation power and demineralization potential, followed by sulfuric acid. By increasing the concentration of nitric acid (0.1–4 mol/L), a significant increase in chromium extraction yield could be observed, because the high proton concentrations of HNO_3 destabilize the strong Cr-Cr bonds between neighboring chromium atoms in the Cr matrix -collagen, but after a certain concentration, a destabilization of the protein structure occurs. The study of the parameters directly involved in the ultrasound stage demonstrated that there is an increase in the chromium extraction yield at low frequencies (25-37 KHz) using the ultrasound bath, but also an increase in extraction with the increase in the applied amplitude (10– 90%). Studies on the influence of temperature (10–90 °C) have shown that there is an improvement in the extraction yield with increasing temperature, but above 30℃, degradation of the protein matrix occurs, as it is well known that collagen denaturation occurs at 37℃ [58].

Also, the influence of ultrasound in presence of on chromium extraction used an organic acid salt (EDTA) was studied [63]. The results demonstrated that ultrasound-assisted extraction leads to a reduction in the extraction time of chromium found in the waste composition (45 minutes). In addition, following the research carried out by them, it was possible to conclude that the extraction yield is significantly influenced by the variation of other parameters involved in the extraction process of chromium from tanned leather waste (extraction temperature, L-S ratio, extraction time). The study of the influence of the S:L ratio (Cr^{3+}: EDTA) showed that the extraction yield improves significantly when the ratio increases (in the range of 1:0-1:6), but the optimal value is 1:3, because in the case of a ratio of 1:6, a similar yield is obtained. The chromium extraction yield follows a similar trend, when the extraction temperature is varied (60℃ to 90℃), but at temperatures higher than 80℃, a degradation of the skin waste was observed, while the variation of the ultrasonication time (30 min-120 min) did not significantly influence the yield [63].

At the same time, a similar study on the influence of ultrasound in presence of an organic acid salt (EDTA) over the extraction yield of Cr (III) was carried out by Pedrotti and collaborators [64]. By studying the influence of the ultrasonic power, the applied temperature, and the contact time, it was possible to observe a directly proportional influence between the increase in the values of these parameters and the amount of chromium extracted from the analyzed leather waste. Increasing the temperature (30-80 °C) led to an increase in the extraction yield, but at temperatures higher than 70 °C, a degradation of the solid skin waste was observed, turning it into a gelatinous fraction. Also, a decrease in contact time and non-breakage temperature to achieve high extraction yields was observed when the ultrasonic power increased. By varying the washing time (3-10 minutes), an insignificant influence on the extraction yield was observed [64].

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

7. Conclusions

The purpose of this review was to present the most current methods used for dechroming solid chrome-tanned leather, in order to reuse it as an alternative raw material in new industrial sectors, by applying the principles of circular economy.

In this study, the latest acid, basic, enzymatic extraction techniques of trivalent chromium were identified based on the hydrolysis method, or on the substitution method, and at the same time, the advantages and disadvantages of each identified method were also discussed. It could be observed that by using the hydrolysis method to extract chromium from tanned leather waste composition, chromium recovery yields between 30-100% can be obtained, but at the same time the collagen matrix can be partially (3-10%) or totally (~100%) destroyed. On the other hand, using the substitution method with the help of organic chelators, were obtained high chromium extraction yields (over 71%), without significantly degrading the collagen matrix, but the purchase costs of the organic reagents used are relatively higher. In addition, it could be observed that by applying the ultrasonic process in the chromium extraction experiments, the extraction time, concentration and amount of reagents are significantly reduced, while the chromium extraction yields exceed 71,7%.

Based on the literature studies carried out, it was possible to conclude that a combination of the hydrolysis and substitution methods with ultrasound process leads to significantly improved chromium removal yields from leather solid waste and a low collagen matrix degradation yield.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, D.S.S. and A.M.N.C.(M).; methodology LK and M.S.; validation, D.S.S., L.K. and M.S.; investigation, A.M.N.C.(M).; resources, D.S.S.; data curation, M.S.; writing—original draft preparation, A.M.N.C.(M).; writing—review and editing, D.S.S. and M.S ; visualization, L.K.; supervision, D.S.S.; All authors have read and agreed to the published version of the manuscript." Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

Funding: This research received no external funding.

Acknowledgments: The work was funded by Ministry of Research, Innovation and Digitalization of Romania through Nucleu Programme through contract 3N/2022, Project PN 23 22 04 01.

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

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