U.P.B. Sci. Bull., Series B, Vol. 87, Iss. 2, 2025 ISSN 1454-2331

PRELIMINARY STUDIES REGARDING CHROMIUM EXTRACTION FROM CHROMIUM-TANNED LEATHER WASTE

Ana-Maria Nicoleta CODREANU (MANEA)[1,], Daniela Simina ȘTEFAN[2],
Lidia KIM[3], Georgiana CERNICA[1,3]

Chromium represents one of the most hazardous pollutants present in the chromium tanned leather waste composition. This fact represents an impediment of direct valorization. The extraction of this pollutant from chromium-tanned leather waste (CTLW) composition allows the reuse of waste as raw material in new industrial processes by applying the circular economy principles. The purpose of this study was to develop a chromium extraction alternative method from CTLW composition, without destroying the collagen matrix. At the same time, the influence of some parameters (extraction agent type, extraction agent concentration, temperature, contact time, number of extraction steps) on the chromium removal efficiency was studied. The comparative study of main chromium extraction methods (the hydrolysis method with sulfuric acid and the substitution method with oxalic acid and sodium oxalate) demonstrated that the substitution method with oxalic acid is the optimal method for chromium removal. Also, the experimental results demonstrated a direct proportional relationship between extraction agent concentration (oxalic acid 2 - 8%), temperature (30 - 90˚C), contact time (50 - 250 min), number of extraction steps (six) and the chromium removal efficiency. Thus, the chromium from CTLW composition can be completely removed by applying the optimal conditions: extraction with oxalic 6.5%, temperature of 60˚C and 100 min contact time, or by applying extraction in six consecutive stages with water- oxalic acid 6.5% - water - EDTA 2% - water - oxalic acid 6.5% at temperature of 35˚C.

Keywords: acid extraction; acid hydrolysis; substitution method, chromium extraction, dechromed leather waste

1. Introduction

Demographic growth studies at the global level show an increase of the number of people by approximately one third until the year 2060 [1-2]. This fact implies the increase in food production, which can be achieved by improving crop yields by applying exponential amounts of fertilizers [3]. Conventional chemical fertilizers have the disadvantage of a low efficiency of use (only 30-35% of the

---

[1] PhD student, Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology POLITEHNICA of Bucharest, Romania, e-mail: anamariacodreanu99@yahoo.com

[2] Prof., Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology POLITEHNICA of Bucharest, Romania, e-mail: daniela.stefan@upb.ro

[3] National Research and Development Institute for Industrial Ecology, Department for Evaluation, Monitoring Environmental Pollution, Bucharest, Romania; lidia.kim@incdecoind.ro

nutrients present in the composition reach the plants), and consequently the high frequency of application, which leads to excessive pollution of the environment [4-5]. Thus, research in the field of fertilizers is based on the development of new fertilizers. Smart fertilizers with controlled release of nutrients are an alternative to conventional fertilizers [6].

By applying the principles of the circular economy, numerous studies have presented the use of leather waste (shavings, fleshings, splits and trimmings) from the leather industry as a raw material in the process of obtaining smart fertilizers [7-11]]. Collagenous leather waste represents an important source of nitrogen (approximately 14%), a fact that allows their use in the composition of intelligent fertilizers [12]. The main problem of these wastes is the presence of dangerous pollutants in their composition, such as chromium (mainly Cr_2O_3 is about 2%-4%) [13-14]. The maximum amount of chromium allowed in the fertilizers composition is 2 mg/Kg for Cr (VI) and 300 mg/Kg for total chromium [15]. In consequence, before being used in the fertilizer's composition, chromium tanned leather waste must be dechromed [16- 17]. The most used dechromation methods are based on the hydrolysis method (acid/basic/enzymatic) and the substitution method with organic chelators (acids/salts of organic acids) [18-24]. During the chromium extraction process, it is very important to remove a large amount of chromium, but without destroying the collagen matrix.

The purpose of this study was to compare the analysis of acid hydrolysis and the substitution method, in order to remove chromium, but without significantly destroying the collagen matrix. Comparative studies of the extraction by the substitution method and the hydrolysis method demonstrated the fact that the substitution method helps to obtain a yield close to 100%. Similar results obtained by the substitution method have been presented in literature. Wang et al obtained a chromium extraction yield of 98% using the substitution method with sodium oxalate 2%, while Popiolski et al obtained a chromium extraction yield of 98% using the substitution method with EDTA [23-24].

2. Materials and methods

2.1. Materials

Chromium-tanned leather shavings (CTLW) were collected from local leather industry, Romania (Fig. 1).

Fig. 1. The appearance of the leather waste sample at different temperatures

Goat tanned leather samples used in the chromium leaching experiments were dried at room temperature until constant mass. The thickness of leather samples was about 3 mm, and the samples were cut into small pieces with a diameter of less than 1 cm. The prepared chromium-tanned leather waste was stored at room temperature for all the chromium extraction experiments. Table 1 presents the chemical composition of chromium tanned leather waste used in our study. The chromium content was determined by Atomic Absorption Spectrometry (AAS), while the other metals metals were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The content of carbon, sulfur, nitrogen was determined using CHNS Elemental Analyzer.

Table 1.

Chemical characteristics of chromium tanned leather waste

No.	**Parameter name**	**Value**	**Standard Methods**	**Bibliography of the STAS**
1	pH- aqueous extract	4.9	EPA 9045D	[25]
2	Water content, %	4.4	SR EN ISO 21660-3:2021-3	[26]
3	Dry substance, %	95.64	SR EN ISO 21660-3:2021-3	
4	Loss of calcination, %	90.6*	SR EN 15935:2021	[27]
5	Ash content, %	9.4*	SR EN ISO 21656: 2021	[28]
6	Total chromium, mg/kg	34950.63*	SR EN 16171:2017	[29]
7	Potassium, mg/kg	35.62*	SR EN 16171:2017	
8	Phosphorus, mg/kg	1298*	SR EN 16171:2017	
9	Arsenic, mg/kg	0.21*	SR EN 16171:2017	
10	Barium, mg/kg	16.65*	SR EN 16171:2017	
11	Cadmium, mg/kg	0.0077*	SR EN 16171:2017	
12	Copper, mg/kg	10.91*	SR EN 16171:2017	
13	Mercury, mg/kg	0.048*	SR EN 16171:2017	
14	Molybdenum, mg/kg	0.73*	SR EN 16171:2017	
15	Nickel, mg/kg	1.96*	SR EN 16171:2017	
16	Stibium, mg/kg	0.04*	SR EN 16171:2017	
17	Selenium, mg/kg	0.11*	SR EN 16171:2017	

18	Zinc, mg/kg	10.98*	SR EN 16171:2017	
19	Carbon, %	48.04*	SR EN ISO 21663:2021	[30]
20	Total organic carbon, %	39.88*	SR EN ISO 15936:2022	[31]
21	Total nitrogen, %	11.68*	SR EN ISO 21663:2021	[30]
22	Hydrogen, %	5.85*	SR EN ISO 21663:2021	[30]
23	Sulphur, %	1.64*	SR EN 15408:2011	[32]

*Values are reported as dry substance

2.2. Experimental procedure

Chromium extraction processes were based on the contact of chromium-tanned leather shavings with three different extraction agents, such as sulfuric acid 5% (H_2SO_4), oxalic acid ($H_2C_2O_4$) 5% and sodium oxalate ($Na_2C_2O_4$) 5%, to obtain the best chromium extraction yield. The influence of other parameters was also investigated: concentration of the extraction agent (oxalic acid 2% - 8%, extraction temperature (30˚C - 90˚C) and contact time (50 - 250 min). Table 2 presents a detailed description of the parameters investigated during extraction studies.

Table 2.

Parameters investigated chromium extraction study from chromium-tanned leather shavings

No.	**Parameter**	**Value**					
1	Extraction agent	Sulfuric acid 5%	Oxalic acid 5%		Sodium oxalate 5%		
2	Concentration of extraction agent (%)	2	3.5	5	6.5	8	
3	Temperature (˚C)	30	45	60	75	90	
4	Contact time (minutes)	50	100	150	200	250	
5	Number of extraction steps	1	2	3	4	5	6

Chromium extraction yield was calculated using the equation:

$$\eta Cr\ extr = (wi-wr)/wi\times 100,$$

where: ***wi*** is the chromium concentration in the initial leather waste sample (mg/kg reported at dry substance); ***wr*** is the concentration of chromium in a residual leather waste sample obtained after the filtration process (mg/kg reported at dry substance); ***ηCr extr*** is chromium extraction yield (%).

The hydrolysis degree of the residue was calculated using the equation:

$$Hyd.\ degree = (wa-wb)/wa\times 100,$$

where***:*** ***wa*** is the mass of initial dry sample (g); ***wb*** is the mass of dry sample after extraction (g); ***Hyd. degree*** is the hydrolysis degree of the residue (%).

2.2.1 Experimental procedure to study the influence of extraction agent

The leather waste sample, prepared in advance according to 2.1 subsection, was subjected to the extraction process by putting it into contact with three different extraction agents (sulfuric acid 5%, oxalic acid 5% and sodium oxalate 5%) in a 250 ml flask. The mixture was stirred using the magnetic stirrer for 150 minutes, at 200 rpm, 60 ˚C temperature and 1:11, solid:liquid ratio (S:L ratio). Finally, the obtained mixture was filtered at atmospheric temperature and the collected filtrate was used to chromium content.

2.2.2 Experimental procedure to study the influence of extraction agent concentration

The leather waste sample, prepared in advance according to 2.2 subsection, was subjected to the extraction process by putting it into contact with oxalic acid at five different concentrations (2%, 3.5%, 5%, 6.5%, 8%) in a 250 ml flask. The mixture was stirred using the magnetic stirrer for 150 minutes, at 200 rpm, 60˚C temperature and 1:11 S:L ratio. Finally, the obtained mixture was filtered at atmospheric temperature and the collected filtrate was used to chromium content determination.

2.2.3 Experimental procedure to study the influence of temperature

The leather waste sample, prepared in advance according to 2.2 subsection, was subjected to the extraction process by putting it into contact with oxalic acid 6.5% at five different temperatures (30˚C, 45˚C, 60˚C, 75˚C, 90˚C) in a 250 ml flask. The mixture was stirred using the magnetic stirrer for 150 minutes, at 200 rpm and 1:11 S:L ratio. Finally, the obtained mixture was filtered at atmospheric temperature and the collected filtrate was used to chromium content determination.

2.2.4 Experimental procedure to study the influence of contact time

The leather waste sample, prepared in advance according to 2.2 subsection, was subjected to the extraction process by putting it into a contact with oxalic acid 6.5% at five different contact times (50 min, 100 min, 150 min, 200 min, 250 min) in a 250 ml flask. The mixture was stirred using the magnetic stirrer at 200 rpm, 60˚C temperature and 1:11 S:L ratio. Finally, the obtained mixture was filtered at atmospheric temperature and the collected filtrate was used to chromium content determination.

2.2.5. Experimental procedure to study the influence of a number of extraction steps

The schematic representation of the extraction process in six steps was presented in Fig 2. In the first stage, the sample was put in contact with distilled water, S:L ratio 1:11, at a temperature of 35˚C, stirring speed 200 rpm, for 30 minutes. At the end of the contact time, the sample was subjected to the atmospheric pressure filtration process.

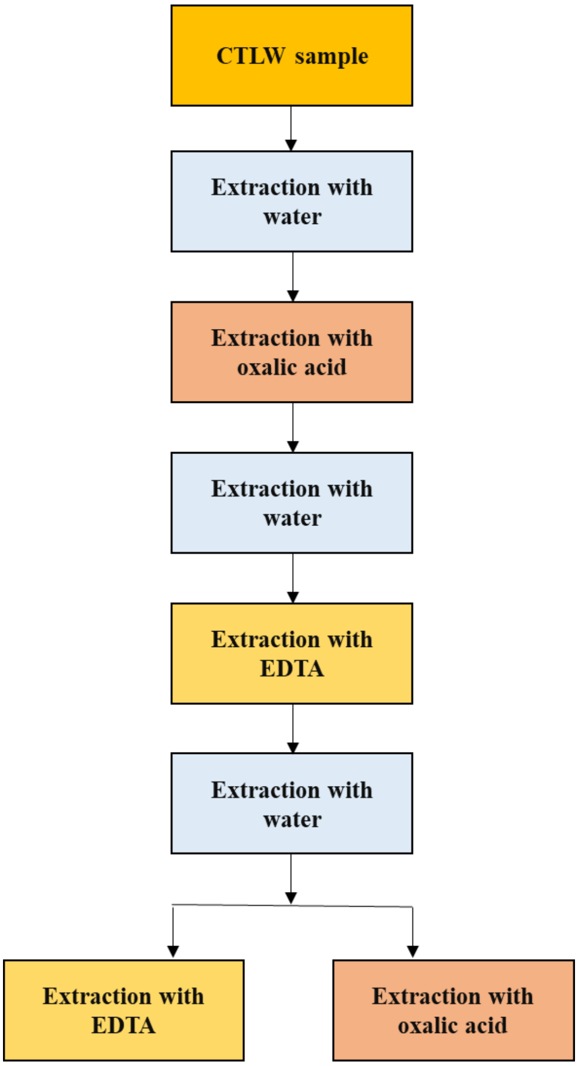

Fig. 2. Schematic representation of the extraction process in six steps.

In the second stage, the residue collected from the first stage was put in contact with 6.5% oxalic acid solution, S:L ratio 1:11 for 100 minutes, stirring speed 200 rpm, at a temperature of 35˚C. At the end of the contact time, the sample was subjected to the filtration process at atmospheric pressure. In the third stage, the collected residue from the second stage was put in contact with distilled water in the S:L ratio 1:11, at temperature of 35˚C, stirring speed 200 rpm, for 30 minutes. At the end of the contact time, the sample was subjected to the atmospheric pressure filtration process. In the fourth stage, the collected residue from the third stage was put in contact with 2% EDTA solution, S:L ratio 1:11 for 100 minutes, stirring speed 200 rpm, at the temperature of 35˚C. At the end of the contact time, the sample was subjected to the filtration process at atmospheric pressure. In the fifth stage, the collected residue from the fourth stage was subjected to the extraction process with distilled water, S:L ratio 1:11, at a temperature of 35˚C, stirring speed 200 rpm, for 30 minutes. At the end of the contact time, the sample was subjected to the atmospheric pressure filtration process. In the last step of the extraction process, the collected residue from the fifth stage was put in contact separately with solutions of EDTA 2%, respectively oxalic acid 6.5%, S:L ratio 1:11 for 100 minutes, stirring speed 200 rpm, at the temperature of 35˚C. At the end of the contact time, the sample was subjected to the filtration process at atmospheric pressure. The filtrates collected in each stage were subjected to a chromium content determination study

3. Results and discussion

3.1. Sample characterization

The chemical characterization of the chromium leather waste sample highlighted the presence of a high chromium content (34.950.63 mg/Kg dry substance). The analysis regarding the nitrogen content revealed the presence of a high nitrogen content (11.68% dry substance) in the composition of the studied waste. Due to the high nitrogen content, which is also primarily sourced from collagen proteins, the sample can be used as an alternative source of nitrogen in new fields, such as the smart fertilizers field. Also, the compositional characterization demonstrated the presence of other nutrients, regularly found in the composition of fertilizers. Primary micronutrients are present: phosphorus (10298 mg/Kg dry substance) and potassium (35.62 mg/Kg dry substance). Secondary macronutrients such as sulfur (1.64% dry substance), as well as trace minerals, such as zinc (10.98 mg/Kg dry substance), copper (10.91 mg/Kg dry substance), molybdenum (0.73 mg/Kg dry substance) are also present.

3.2. Effect of extraction agents

The influence of studies of the three extraction agents on the chromium removal efficiency from CTLW demonstrated a major difference depending on the extraction agent type. The results regarding chrome removal efficiency, hydrolysis degree of residue, as well as the pH samples variation, before and after extraction, are presented in Table 3.

Table 3.

The results obtained using three different extraction agents

Description of the experiment	Initial pH	Final pH	Extraction yield (%)	Hydrolysis degree (%)
CTLW treated with sulfuric acid 5%	0.47	0.82	5.65	1.95
CTLW treated with oxalic acid 5%	0.65	1.04	66.55	1.12
CTLW treated with sodium oxalate 5%	6.04	5.76	9.12	1.03

By applying the hydrolysis method using sulfuric acid, only 5.65% of the chromium present in the CTLW composition was removed. By applying the substitution method with oxalic acid, as an organic chelator, the best chromium removal yield was obtained, 66.55%.

In contrast, the results of chromium removal yield using sodium oxalate were found. The chromium extraction by substitution method with sodium oxalate led to obtaining a poor extraction yield of only 9.12%. The yields variation depending on the three extraction agents used was presented in Fig. 3. The experimental results obtained demonstrated that the optimal chromium removal agent from the goat skin waste composition is oxalic acid. Also, the results regarding the hydrolysis of leather waste demonstrated that the three tested agents do not hydrolyze the sample (hydrolysis degree under 2%) during the extraction process.

3.3. Effect of oxalic acid concentration

The variation of oxalic acid concentration in the range of 2-8% demonstrated a directly proportional relationship between acid concentration and the chromium extraction yield. The results regarding the initial pH of the samples treated with oxalic acid, the final pH of the sample, the hydrolysis degree of residue and the extraction yields obtained in our experiments are shown in Table 4. After putting the CTLW samples in contact with different concentrations of oxalic acid, in all studied cases, a decrease in the solutions pH could be observed.

Table 4.

The results obtained using different concentration of oxalic acid.

Description of the experiment	Initial pH	Final pH	Extraction yield (%)	Hydrolysis degree (%)
CTLW treated with oxalic acid 2%	1.51	1.50	27.17	0.98
CTLW treated with oxalic acid 3.5%	1.31	1.25	54.47	1.06
CTLW treated with oxalic acid 5%	1.24	1.10	66.99	1.12
CTLW treated with oxalic acid 6.5%	1.15	0.97	88.28	2.20
CTLW treated with oxalic acid 8%	1.06	0.93	85.27	4.57

As it can be seen in Fig. 4, the extraction yield increases with the increase of oxalic acid concentration in the range of 2%-8%. The best chromium extraction (88.28%) yield from CTLW composition was obtained at 6.5% oxalic acid concentration. After this optimal concentration, a decrease in chromium ex-traction yield could be observed. At 8% oxalic acid concentration, the removal yield was 85.27%, a similar value to 6.5% concentration. However, at the concentration of 8%, a higher degree of hydrolysis of the residue could be observed (4.57%). In consequence in the following studies, oxalic acid 6.5% was used as the optimal agent for chromium extraction from tanned leather waste composition.

3.4. Effect of temperature

The influence of the study of temperature on the chromium extraction yield demonstrated that temperature plays a key role in the extraction process. The results regarding the initial pH of the samples treated with oxalic acid 6.5% at room temperature, the final pH of the sample after applying the temperature, hydrolysis degree of the residue and the extraction yields obtained in our experiments are shown in Table 5.

Table 5.

The results were obtained using different temperatures.

Description of the experiment	Initial pH	Final pH	Extraction yield (%)	Hydrolysis degree (%)
CTLW treated at 30˚C	1.24	1.16	43.38	0.45
CTLW treated at 45˚C	1.24	1.19	55.72	1.98
CTLW treated at 60˚C	1.24	1.36	88.30	2.20
CTLW treated at 75˚C	1.24	0.98	95.19	14.65
CTLW treated at 90˚C	1.24	0.93	99.49	69.26

The results regarding the pH variation demonstrated an inverse proportional relationship between temperature and pH during the extraction process. Therefore, as the temperature increases between 30˚C - 90˚C, the pH of the samples decreases, becoming strongly acidic (0.93). At the same time, the results obtained demonstrated an increase of chromium extraction yield from the CTLW composition with the temperature increases (Fig. 5). At a temperature of 30˚C, less than half of chromium amount (chromium extraction yield was 43.38%) was extracted while at a temperature of 90˚C almost all the chromium was extracted from the chromium-collagen matrix chromium extraction yield was 99.49%). However, it could be observed that after the temperature of 60˚C the sample hydrolyzes, the degree of hydrolysis at 90˚C being 69.26%. At the end of the experimental studies, it was concluded that the temperature of 60℃ represents the optimal extraction temperature (chromium extraction yield 88.30% and hydrolysis degree of residue 2.20%). In consequence in the following studies, the temperature of 60˚C was used as the optimal temperature in the chromium extraction process from the composition of tanned leather waste.

3.5. Effect of contact time

The results obtained after putting in contact the samples with 6.5% oxalic acid for different periods of time are presented in Table 6. As it can be seen in Fig. 6, in just 100 min contact time, it extracts around 90% of the chromium present in the CTLW composition.

Table 6.

The results were obtained using different contact times

Description of the experiment	Initial pH	Final pH	Extraction yield (%)	Hydrolysis degree (%)
CTLW at 50 min	1.24	1.07	56.85	1.78
CTLW at 100 min	1.24	0.96	87.49	2.14
CTLW at 150 min	1.24	0.93	88.42	2.20
CTLW at 200 min	1.24	0.89	89.08	4.62
CTLW at 250 min	1.24	0.77	90.32	5.09

The lowest extraction yield was obtained after 50 min contact time (56.85%), which indicated that a contact time of 50 min is not sufficient to extract the entire amount of chromium present in the tanned leather waste.

At the opposite pole were the extraction yields obtained after 250 min. Consequently, it could be observed that the values regarding the chromium extraction yield in the time interval 100 min-250 min are close, but the degree of hydrolysis of the residue in this interval increases (2.14% to 5.09%). At the end of our studies, we concluded that the optimal contact times can be 100 min and 150 min. Considering the time saving, it can be considered that 100 min represents the optimal extraction time.

3.6. Effect of the number of extraction steps

The studies regarding the application of successive stages of chromium extraction in order to obtain the highest extraction yield have revealed that the extraction yield can be improved by increasing the number of extraction stages. The results regarding the extraction yields obtained after each cycle are presented in Table 7.

Table 7.

The results obtained using six consecutive extraction stage.

Description of the experiment	Extraction yield (%)	Hydrolysis degree (%)
Extraction with water	0.041	0.35
Extraction with water - oxalic acid 6.5%	43.48	0.45
Extraction with water- oxalic acid 6.5%-water	48.17	0.96
Extraction with water- oxalic acid 6.5%-water-EDTA 2%	86.67	3.09
Extraction with water- oxalic acid 6.5%-water-EDTA 2%-water	88.33	3.48
Extraction with water- oxalic acid 6.5%-water- EDTA 2%-water-EDTA 2%	90.82	5.55
Extraction with water- oxalic acid 6.5%- water- EDTA 2%-water-oxalic acid 6.5%	98.95	3.96

The experimental results obtained demonstrated that through the application during the first stage of water extraction, a small amount of chromium is extracted (below 0.05%).

During the study, it was also possible to observe the fact that water extraction does not lead to the extraction of a large amount of chromium (maximum 5% chromium extracted). After applying two consecutive stages of extraction, the first with water and the second with 6.5% oxalic acid, a significant increase in the extraction yield was observed (extraction yield 43.48%). In addition, following the third step with water and the fourth extraction step with 2% EDTA, a doubling of the amount of chromium extracted (extraction yield 86.67%) was observed.

By applying in the fifth stage the extraction of chromium with water and in the sixth stage the extraction of chromium with EDTA 2% led to the improvement of the extraction yield by four percent, and the final yield obtained was 82%.

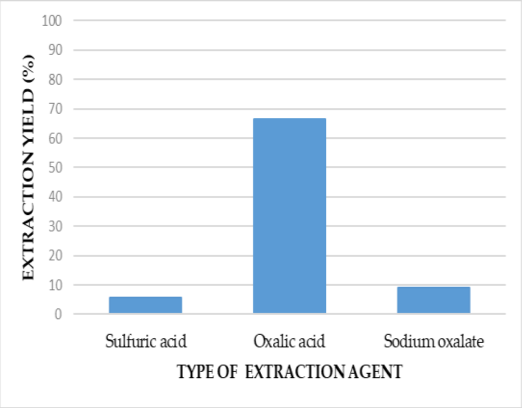

Fig 3. The influence of the type of extraction agent

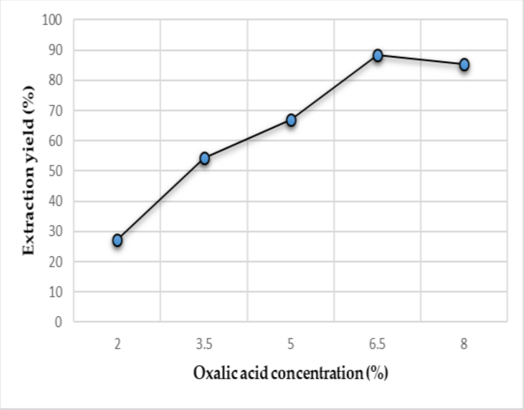

Fig 4. The influence of the oxalic acid concentration

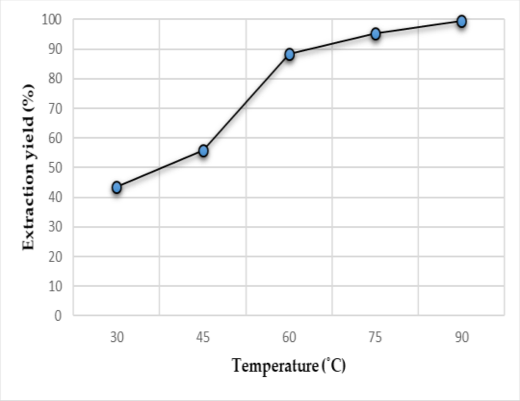

Fig 5. The influence of temperature

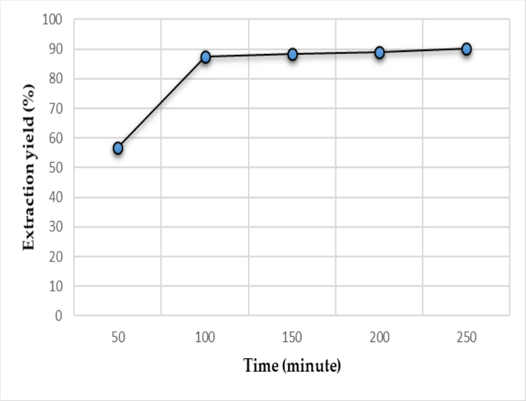

Fig 6. The influence of time

On the other hand, by applying in the fifth stage of the extraction of chromium with water and in the sixth stage the extraction of chromium with oxalic acid 6.5%, the best chromium extraction yield was obtained (98.95%).

In addition, the results regarding the hydrolysis degree demonstrated the fact that the successive application of the extraction steps increases the hydrolysis of the residue. The highest degree of hydrolysis of waste (5.55%) was recorded by applying EDTA in the sixth stage of extraction. At the same time, by applying oxalic acid in the sixth stage of ex-traction, the degree of hydrolysis of the residue was 3.96%. Thus, the optimal conditions were the application of six extraction stages based on water - oxalic acid 6.5% - water- EDTA 2% - water- oxalic acid 6.5% extraction.

6. Conclusions

Removal of chromium from the CTLW composition represents the first step to reusing this waste in new industrial processes. The present study presented an alternative method of removing the chromium present in leather waste composition, without destroying the collagen matrix. The research carried out has demonstrated the ability to obtain a chromium extraction yield of 87.49% and a low hydrolysis degree of residue (2.14%), using optimal conditions of 60 ˚C temperature, 100 min contact time, 6.5% oxalic acid concentration, S:L ratio 1:11, stirring speed 200 rpm. Also, by applying six extraction stages with water- oxalic acid 6.5% - water - EDTA 2% - water - oxalic acid 6.5% at a temperature of 35 ˚C, stirring speed 200 rpm, S:L ratio 1:11, the best chromium extraction yield of 98.95% and a hydrolysis degree of residue of 3.96% were obtained.

REFERENCES

[1]. *Food and Agriculture Organization of the United Nations, Food Security and Nutrition in the Age of the Climate Change*, International Symposium organized by the government of Québec in collaboration with FAO, Québec City, September 24-27, 2017.

[2]. *D. Lawrencia, S. K. Wong, D. Y. S. Low, B. H. Goh, J. K. Goh,* Controlled Release Fertilizers: A Review on Coating Materials and Mechanism of Release, Plants, **vol. 10**, 2021,1-25.

[3]. *B. Sekhon*, Nanotechnology in agri-food production: an overview, Nanotechnology, Science and Applications, **vol. 7**, 2014, 31-53.

[4]. *P. Vejan, T. Khadiran, R. Abdullah, N. Ahmad*, Controlled release fertilizer: A review on developments, applications and potential in agriculture, Journal of Controlled Release, **vol. 339**, 2021, 321-334.

[5]. *A. Ditta, M. Arshad*, Applications and perspectives of using nanomaterials for sustainable plant nutrition, Nanotechnology Reviews, **vol. 5**, 2016, 209-229.

[6]. *M.E. González, M. Cea, J. Medina, A. González, M.C. Diez, P. Cartes, Monreal, R. Navia*, Evaluation of biodegradable polymers as encapsulating agents for the development of a urea controlled-release fertilizer using biochar as support material, Science of The Total Environment, **vol. 505**, 2015, 446-453.

[7]. *M. Sathish, B. Madhan, J. R. Rao*, Leather solid waste: An eco-benign raw material for leather chemical preparation – A circular economy example, Waste Management, **vol. 87**, 2019, 357-367.

[8]. *J. Kanagaraj, T. Senthilvelan, R.C. Panda, S. Kavitha*, Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: a comprehensive review, Journal of Cleaner Production, **vol. 89**, 2015, 1-17.

[9]. *V. Muralidharan, S. Palanivel, M. Balaraman*, Turning problem into possibility: A comprehensive review on leather solid waste intra-valorization attempts for leather processing, Journal of Cleaner Production, **vol. 367**, 2022, 133021.

[10]. *S. Zhou, L. X. Zhou, S. M. Wang, D. Fang*, Removal of Cr from tannery sludge by bioleaching method, J Environ Sci (China), **vol. 18**, 2006, 885-890.

[11]. *D.S. Stefan, M. Bosomoiu, R. R. Constantinescu, M. Ignat*, Composite Polymers from Leather Waste to Produce Smart Fertilizers, Polymers, **vol. 13**, 2021, 4351.

[12]. *A. Malek, M. Hachemi, V. Didier*, New approach of depollution of solid chromium leather waste by the use of organic chelates: Economical and environmental impacts, Journal of Hazardous Materials, **vol. 170**, 2009, 156-162.

[13]. *L. Wang, J. Li, Y. Jin, M.Chen, J. Luo, X. Zhu, Y. Zhang,* Study on the removal of chromium (III) from leather waste by a two-step method, Journal of Industrial and Engineering Chemistry, **vol. 79**, 2019, 172-180.

[14]. *L. Peng, W. Long, W. Zhang, B. Shi*, Leaching toxicity and ecotoxicity of tanned leather waste during production phase, Process Safety and Environmental Protection, **vol. 161**, 2022, 201-209.

[15]. *A.F. Burg, G. M. Hiedrich, A. Viana, V. L.Dressler*, Chromium speciation in organic fertilizers by spectrophotometry, Quím. Nova, **vol. 48**, 2025.

[16]. *A. M. N. Codreanu (Manea), D. S. Stefan, L. Kim, M. Stefan,* Depollution of Polymeric Leather Waste by Applying the Most Current Methods of Chromium Extraction, Polymers, **vol. 16**, 2024, 1546.

[17]. *K. Chojnacka, D. Skrzypczak, K. Mikula, A. Witek-Krowiak, G. Izydorczyk, K. Kuligowski, P. Bandrów, M. Kułażyńsk*i, Progress in sustainable technologies of leather wastes valorization as solutions for the circular economy, Progress in sustainable technologies of leather wastes valorization as solutions for the circular economy, **vol. 313**, 2021, 127902.

[18]. W. Ding, L. Xuepin, W. Zhang, B. Shi, Dechroming of Chromium-containing Leather Waste with Low Hydrolysis Degree of Collagen, Journal- Society of Leather Technologists and Chemists, **vol. 99**, 2015, 129-133. Sichuan University

[19]. *B. Wionczyk, W. Apostoluk, W. Charewicz, Z. Adamski*, Recovery of chromium(III) from wastes of uncolored chromium leathers. Part I. Kinetic studies on alkaline hydrolytic decomposition of the wastes, Separation and Purification Technology, **vol 81**. , 2011, 223-236.

[20]. *M. Ferreira, M. Almeida, S. Pinho, I. Santos*, Finished leather waste chromium acid extraction and anaerobic biodegradation of the products, Waste Management, **vol. 30**, 2010, 1091-1100.

[21]. *A. Dettmer, R. M. Oliveira dos Santos, P. Schacker dos Anjos, M.Gutterres*, Protein extraction from chromium tanned leather waste by Bacillus subtilis enzymes, Journal of AQUIEC, **vol. 65,** 2014, 93-100.

[22]. *X. Qiang, H. Feng,* Collagen extracted from chrome shavings using alkali and Enzyme, 2011 International Conference on Remote Sensing, Environment and Transportation Engineering.

[23]. *L. Wang, M. Chen, J. Li, Y. Jin, Y. Zhang, Y. Wang,* A novel substitution-based method for effective leaching of chromium (III) from chromium-tanned leather waste: The thermodynamics, kinetics and mechanism studies, Waste Management, **vol. 103**, 2020, 276-284.

[24]. *A. Popiolski, R. Dallago, J. Steffens, M. Mignoni, L. Venquiaruto, D. Santos, F. Duarte,* Ultrasound-Assisted Extraction of Cr from Residual Tannery Leather: Feasibility of Ethylenediaminetetraacetic Acid as the Extraction Solution, ACS Omega, **vol. 3**, 2018, 16074-16080.

[25]. *U.S. Environmental Protection Agency,* METHOD 9045D SOIL AND WASTE pH, Revision 4, November 2004, efaidnbmnnnibpcajpcglclefindmkaj/https://www.epa.gov/sites/default/files/2015-12/documents/9045d.pdf.

[26].*ISO STANDARDS*, Solid recovered fuels — Determination of moisture content using the oven dry method, Part 3: Moisture in general analysis sample, Ed.1, 2021, https://www.iso.org/standard/71327.html.

[27]. *SLOVENSKI STANDARD SIST*., Soil, waste, treated biowaste and sludge - Determination of loss on ignition, 2021, https://standards.iteh.ai/catalog/standards/cen/04a0cbb3-843f-466a-bb39-39217af45d51/en159352021?srsltid=AfmBOopwVWgQ8VdHBG23T6KxizmldLxMFoxGOQrAAY-etybk4CVP5MZv.

[28]. *ISO STANDARDS,* Solid recovered fuels — Determination of ash content, Ed.1, 2021, https://www.iso.org/standard/71321.html.

[29]. *SLOVENSKI STANDARD SIST*, Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS), 2017, https://standards.iteh.ai/catalog/standards/sist/b5dbe9bc-669b-4cb6-8a58-b318e359d178/sisten161712017?srsltid=AfmBOooTTzc51_E3G35UCAgRIcv1dhrW47cgfi93f-goMmziarufgoRC.

[30]. *SLOVENSKI STANDARD SIST*, Solid recovered fuels - Methods for the determination of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method, 2020, https://standards.iteh.ai/catalog/standards/cen/e357a81413994bd4bbc78f7eca1142d/eniso216632020?srsltid=AfmBOooFSc7Hj3hwIzIZl_t0DrrYIat_oxuUrZMGOnLmM4unMA37BqL.

[31]. *SLOVENSKI STANDARD SIST*, Soil, waste, treated biowaste and sludge - Determination of total organic carbon (TOC) by dry combustion, 2022, https://standards.iteh.ai/catalog/standards/cen/aa80a8830b774f9abf7c98f80c275266/en159362022?srsltid=AfmBOoqWamSzKYtAdotPC6gqwnaX_5Yqlry0vBKrdKGBj5RSdYPBjDc

[32]. *SLOVENSKI STANDARD SIST*, Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content, 2011, https://standards.iteh.ai/catalog/standards/cen/a161797aa88d4fba9d81ee017a66c9ec/en154082011?srsltid=AfmBOoobKDtS8B4FMSq6JTouaJHgz4BZgbH8ueUM7L04H2ViY7p8Lt4.