

## HIGH-EFFICIENCY CHROME TANNING: REDUCING WATER INPUT IN LEATHER PROCESSING

#### SEL Gullu<sup>1</sup>, YORGANCIOGLU Ali<sup>1</sup>, ONEM Ersin<sup>1</sup>

<sup>1,</sup> Ege University, Department of Leather Engineering, İzmir, Türkiye

Corresponding author: Onem Ersin, E-mail: ersin.onem@ege.edu.tr

Abstract: In today's industrial landscape, minimizing environmental impact is a growing priority, particularly in water and chemical-intensive sectors like leather production. One of the main challenges in chrome tanning is the low chromium uptake, with only 40–60% of the tanning agent binding to collagen fibers resulting in significant chromium discharge. This study focuses on improving chrome exhaustion by optimizing water usage in the tanning process. Experimental tanning trials were conducted with reduced water ratios. Following the tanning process, chromium oxide concentration and conductivity were measured in the wastewater. Additionally, the chromium content and shrinkage temperature of the tanned leathers were analyzed to evaluate tanning processes. Findings revealed that decreasing the water ratio can significantly enhance chromium uptake, reduce environmental impact, and maintain or improve the performance of the final leather product, supporting the development of more sustainable tanning technologies.

Key words: Chrome tanning, chromium exhaustion, leather wastewater, sustainable leather processing, water ratio optimization

#### 1. INTRODUCTION

The leather industry heavily relies on large volumes of water and various chemical agents to convert raw hides into finished leather through complex chemical modifications of collagen. This transformation involves multiple stages, including liming, pickling, tanning, and post-tanning operations, each of which consumes considerable amounts of water and contributes to the generation of polluted effluents. However, this conventional production approach generates a substantial amount of highly polluted wastewater, posing significant environmental threats. The presence of organic matter, sulfides, ammonium compounds, and heavy metals like chromium in these effluents has raised concerns over their discharge into natural water bodies. Therefore, reducing the use of both water and chemicals during leather processing is vital for environmental protection, resource conservation, and the sustainability of leather manufacturing [1].

In response to the increasing awareness of environmental and human health concerns, stricter regulations and limitations on the use of hazardous substances in leather production have been introduced [2]. Particularly in developed countries, initiatives have been taken to evaluate the environmental impact of chemicals, develop predictive models, establish chemical databases, and implement process designs aligned with the principles of sustainable production. The REACH regulation is one such effort, aimed at improving chemical safety, enhancing risk management, and



promoting alternative assessment methods. These regulatory frameworks encourage manufacturers to shift toward greener formulations and safer process routes. Despite these efforts, both the presence of hazardous residues in finished leather products and the discharge of chemical-laden wastewater remain pressing issues that hinder sustainable leather production [3].

Achieving zero-waste production is essential to advancing a cleaner and healthier environment. Accordingly, the adoption of cleaner production strategies centered around the principles of "reduce, reuse, and recycle" has become increasingly important. Cleaner production not only aims to minimize pollutant generation at the source but also promotes the reuse of process streams and by-products within the production cycle. International organizations are also promoting the transition to green and low-carbon economies, supporting innovations in closed-loop processing and energy-efficient technologies [4]. Reports on water use in the leather industry indicate that producing 1 ton of leather consumes approximately 35–50 tons of water, leading to an estimated annual wastewater output of  $1.0 \times 10^8$  tons [5]. This figure has recently increased to about  $1.6 \times 10^8$ tons [6], reinforcing the urgent need to develop water-saving solutions across all stages of leather manufacturing.

A critical aspect of the tanning process is the effective penetration and fixation of the tanning agent within the collagen fiber matrix of the hide. However, studies have consistently shown that the uptake of tanning agents under conventional aqueous processing conditions remains inefficient. Typically, only 50–60% of the chromium offered is fixed within the leather, while the remainder is discharged into wastewater, representing both an environmental burden and a financial loss. Significant portions of the tanning agents, particularly chromium salts, remain in the process bath, contributing to pollution loads [7]. Research indicates that exhaustion rates in conventional tanning are relatively low, resulting in high volumes of wastewater contaminated with unconsumed tanning agents. With chrome tanning still accounting for approximately 90% of global leather production, the environmental implications are substantial [8].

Globally, the leather industry uses nearly 500,000 tons of chromium (III) salts annually. With a tanning efficiency of just 55–65% under current methods, nearly half of the chromium applied ends up in wastewater [9]. This inefficient use of chrome not only results in economic loss but also contributes to chromium-related environmental concerns. Despite various studies focusing on alternative tanning agents [10], these substitutes have generally failed to match the hydrothermal stability and physical performance of chrome-tanned leather [11-12]. For this reason, chrome tanning remains indispensable to large-scale leather production. Consequently, approaches that retain chrome use while minimizing environmental risks particularly by improving fixation efficiency and reducing chemical load in wastewater—may be more viable and practical for widespread industry adoption.

Although numerous efforts have focused on post-process wastewater treatment [13], relatively little research has addressed the reduction of water usage during the process itself. Most wastewater solutions have concentrated on end-of-pipe treatments, which, although helpful, are energy-intensive and do not address the root cause of pollution. While suggestions have been made to lower water consumption for sustainability, few practical strategies have been developed to ensure sufficient chemical penetration under reduced water conditions [13]. Therefore, developing efficient in-process solutions that reduce float volume without compromising leather quality is an emerging necessity. As such, previous efforts have been limited in both scope and effectiveness, and have not been widely implemented in commercial practice.

In light of these challenges, the present study aims to address the inefficiencies of conventional chrome tanning by designing novel tanning recipes that significantly reduce both water and chromium tanning agent consumption. By developing high exhaustion chrome tanning systems,



this research seeks to evaluate the resulting leather properties and wastewater characteristics, and to identify the most effective formulations through optimization studies. Ultimately, the study aims to support the transition to more sustainable tanning processes that maintain leather quality while minimizing environmental impact. These efforts align with the global push toward circular resource use, cleaner industrial practices, and compliance with future environmental legislation.

## 2. EXPERIMENTAL

## 2.1. Materials

Pickled sheepskins obtained from the commercial domestic market were used as the raw material for tanning experiments in the conventional process.

## 2.2. Recipes for experiments

Prior to the tanning process, a depickling process was carried out. The formulation used for depickling is presented in Table 1.

Process	%	Substances	Temperature (°C)	Time (min.)	Remarks
Depickling	150	Water	25	20	7-8 Bé
	1.5	HCOONa		40	рН: 4.0
	0.6	NaHCO <sub>3</sub>		45	pH 5.5, drain
Bating	100	Water			
	1.5	Acidic bating agent	35	60	Drain
Washing	200	Water	30	10	Drain
Degreasing	6	Degreasing agent	28	60	
	50	Water (3 Bé)	28	90	Automatic for night, drain
Washing x 3	200	Water	30	30	Drain

Table 1: Depickling recipe

Following the depickling process, conventional chromium tanning was applied to the skins. The tanning formulation is provided in Table 2.

 Table 2: Conventional chromium tanning process

Process	%	Substances	Temperature (°C)	Time (min.)	Remarks
Pickling	100	Water	30	20	6-7 Bé
	1.5	$H_2SO_4$		Run overnight	pH 3.0
	0.1	Fungicide		20	
Chrome tanning	4	Chromium salt		60	
	1	Synthetic fatliquoring agent			
	4	Chromium salt		600	10 hours
	1	HCOONa		45	
	0.8	NaHCO <sub>3</sub>		90	pH 4.2, drain
Washing x 2	100	Water	30	20	Drain



In the high-exhaustion tanning system, the chromium application level was reduced from 8% to 5% to improve efficiency. To optimise water usage, experiments were conducted using water levels of 80%, 60%, and 40%. The recipe employed in these trials is presented in Table 3, where the water usage levels are denoted by the variable X.

Process	%	Substances	Temperature(°C)	Time(min.)	Remarks
Tanning	Х	Water			X:80-60-40
	0.25x2	НСООН		60	рН: 5.0-5.2
	5	Chromium salt			
	0.25	Masking agent		60	
	1	Electrolyte stable fatliquor		30	
Next morning			50	60	рН 5.2
Washing x 2	100	Water	30	20	Drain

Table 3. High chrome exhaustion tanning recipe

#### 2.3. Shrinkage temperature analyses

Shrinkage temperature was determined in accordance with TS 4120 EN ISO 3380. Rectangular samples (50 mm  $\times$  3 mm) were prepared, and a 1:3 glycerol–water mixture at 65°C was used as the test medium. The temperature was increased at a controlled rate of 2°C per minute, and the shrinkage point was identified as the temperature at which significant contraction occurred. Readings were taken every 30 seconds, and the shrinkage temperature was defined based on the movement of the indicator needle.

#### 2.4. Chrome oxide (Cr<sub>2</sub>O<sub>3</sub>) analyses

The chromium oxide content in leather was determined in accordance with TS EN ISO 5398-1, while its concentration in wastewater was analysed following the SLC 208 procedure.

#### **2.5.** Conductivity and salinity analyses

Conductivity and salinity analyses of the waste float water following the tanning process were performed using a YSI Incorporated (Yellow Springs Instrument) device. In cases where the conductivity and salinity values exceeded the instrument's measurement range, the floats were diluted at predefined ratios to allow accurate readings, and final values were calculated by accounting for the dilution factor. Conductivity was expressed in millisiemens per centimeter (mS/cm), and salinity in parts per thousand (ppt).

#### **2.6. Statistical evaluations**

For all experimental trials, two sheepskins were placed into the same drum to ensure uniform processing conditions, and each tanning formulation was repeated in three independent production cycles to achieve replication. As a result, a total of six leather samples (2 skins  $\times$  3 replicates) and three corresponding residual float samples were obtained for each test condition. All analytical measurements including chromium oxide content, shrinkage temperature, conductivity, and salinity were performed on these replicated samples to ensure statistical reliability. The mean values and standard deviations of the data sets were calculated using the SPSS 15.0 statistical software package to assess the consistency and reproducibility of the results.



#### **3. RESULTS AND DISCUSSION**

The increasing global focus on sustainable production has underscored the importance of scientific studies aimed at saving water and energy, and ensuring the efficient use of raw materials and natural resources. Within the scope of environmentally friendly leather processing, many studies emphasize the development of technologies that reduce water and chemical consumption. Nevertheless, research efforts targeting water saving in leather production have often fallen short of providing sufficiently effective outcomes or translating laboratory findings into industrial applications [14].

In this study, rather than completely eliminating water from the tanning process, a high exhaustion chrome tanning system was developed with the goal of minimizing water use without compromising leather quality. Preliminary trials revealed that eliminating water entirely caused undesirable effects like heating on fiber structure and leather integrity due to inadequate lubrication and tanning agent mobility. Based on these observations, the experimental focus shifted toward identifying the lowest possible water usage levels that still allow effective tanning reactions and maintain leather performance characteristics. The results obtained from the conventional chrome tanning method were compiled and are presented in Table 4, serving as a baseline reference to evaluate the efficiency and environmental advantages of the high exhaustion system tested at different reduced water ratios, as given in Table 5.

Analyses	Conventional tanning results
$Cr_2O_3\%$	$2.91\pm0.88$
Shrinkage temperature (°C)	$103 \pm 1.50$
Cr <sub>2</sub> O <sub>3</sub> (residual float) (g/L)	$4.4\pm0.56$
Conductivity (mS/cm)	$121.6 \pm 14.25$
Salinity (ppt)	$98.2 \pm 9.24$

Table 4: Characteristics of leather and wastewater after conventional chrome tanning

As can be seen from Table 4, the shrinkage temperature of the leathers produced by the conventional chrome tanning system was determined to be  $103 \pm 1.50$  °C. This result reflects that the leather structure has been adequately stabilized by the chrome tanning agent and shows typical thermal behavior for chrome-tanned leathers.

The Cr<sub>2</sub>O<sub>3</sub> content in the leather was found to be  $2.91 \pm 0.88\%$ , which is slightly lower. This moderate Cr<sub>2</sub>O<sub>3</sub> content suggests that although tanning occurred, the level of chromium uptake into the leather matrix was not maximized. This could be attributed to relatively low float exhaustion levels typical of conventional tanning, where chromium penetration and fixation are limited by bath concentration and diffusion gradients. Supporting this point, the residual chromium oxide concentration in the float after tanning was measured as  $4.4 \pm 0.56$  g/L, which indicates significant unutilized chromium remaining in the bath. This relatively high residual content is a critical drawback of conventional chrome tanning, highlighting inefficient chemical uptake and environmental concerns due to higher chromium loads in the effluent.

In addition, the conductivity of the residual float was recorded as  $121.6 \pm 14.25$  mS/cm, and salinity as  $98.2 \pm 9.24$  ppt. These high values reflect the substantial presence of dissolved salts and electrolytes in the spent float, which can arise from salt additives used during pickling. High conductivity and salinity levels are important indicators of environmental impact, especially in terms of wastewater treatment challenges. Altogether, the data in Table 4 confirms that conventional chrome tanning results in acceptable leather quality in terms of shrinkage temperature but suffers



from inefficiencies in chrome fixation and significant environmental burden due to high residual chromium, conductivity, and salinity in wastewater.

<b>Tuble 5.</b> Then exhausted tunning processes at afferent water ratios						
Analysis	80% water	60% water	40% water			
Cr <sub>2</sub> O <sub>3</sub> % (leather)	$4.13\pm0.14$	$4.27\pm0.19$	$3.68\pm0.46$			
Shrinkage temperature (°C)	$102.5\pm1.25$	$102\pm0.71$	$102 \pm 1.23$			
$Cr_2O_3$ (residual float) (g/L)	$0.88\pm0.15$	$0.65\pm0.12$	$0.61 \pm 0.44$			
Conductivity (mS/cm)	$54.2 \pm 2.3$	$45.7\pm3.5$	$44.8 \pm 1.6$			
Salinity (ppt)	$38.4\pm2.5$	$40.2\pm1.7$	$40.7\pm2.3$			

Table 5: High exhausted tanning processes at different water ratios

Table 5 illustrates the results of high exhaustion chrome tanning processes carried out at different water use levels (80%, 60%, and 40%), and the findings clearly demonstrate the effectiveness of high pH based exhaustion system with water reduction strategies in increasing chrome uptake and reducing effluent pollution.

At 80% water usage, the Cr<sub>2</sub>O<sub>3</sub> content in leather was determined as  $4.13 \pm 0.14\%$ , which is substantially higher than that achieved in the conventional system (2.91%). The shrinkage temperature was  $102.5 \pm 1.25$  °C, which is very close to the conventional system and confirms that the leather achieved comparable thermal stability despite using less water and a different process approach.

The residual chromium oxide in the float was found to be  $0.88 \pm 0.15$  g/L, significantly lower than the value observed in the conventional system (4.4 g/L). This indicates a highly efficient exhaustion process with improved chromium fixation and a corresponding reduction in environmental load. When the water usage was decreased to 60%, the Cr<sub>2</sub>O<sub>3</sub> content in leather increased slightly to  $4.27 \pm 0.19\%$ , representing the highest chromium uptake among all conditions tested. This value strongly suggests that moderate reduction in water can enhance chromium diffusion and fixation due to more concentrated reaction conditions. The shrinkage temperature remained high at  $102 \pm 0.71$  °C, indicating that structural stabilization was effectively achieved. The chromium content in the residual float decreased further to  $0.65 \pm 0.12$  g/L, supporting the conclusion that 60% water usage provided optimal exhaustion performance in terms of both leather quality and environmental output.

At the lowest water usage level of 40%, the Cr<sub>2</sub>O<sub>3</sub> content in the leather decreased to  $3.68 \pm 0.46\%$ , although it still exceeded the conventional system's chromium content. The shrinkage temperature remained stable at  $102 \pm 1.23$  °C, indicating that tanning was still effective. The chromium oxide remaining in the float was  $0.61 \pm 0.44$  g/L, the lowest among all conditions, which may reflect better exhaustion in low-moisture environments. While the exhaustion appears very efficient, the slightly lower Cr<sub>2</sub>O<sub>3</sub> in leather suggests that under extreme water reduction, the diffusion of chromium into the hide matrix becomes more difficult, possibly due to limitations in mobility within the reduced aqueous phase. Conductivity values in the residual float showed a clear downward trend with decreasing water: from  $54.2 \pm 2.3$  mS/cm at 80% to  $45.7 \pm 3.5$  mS/cm at 60% and  $44.8 \pm 1.6$  mS/cm at 40%. These results indicate a lower ionic concentration in the wastewater, which aligns with the more efficient utilization of tanning chemicals. However, salinity values remained relatively stable across all trials, ranging between 38.4–40.7 ppt, possibly due to retained salt residues from previous processing stages.

The data in Table 5 highlights that the high exhaustion system is capable of achieving better chromium fixation, lower chromium waste, and comparable leather quality even when the float volume is significantly reduced. Among the tested conditions, 60% water usage appears to be the



most favorable, delivering the highest chromium uptake in leather, low residual chromium in the float, and high shrinkage temperature, thereby offering an optimal balance between performance and sustainability. While 40% water usage also showed excellent exhaustion efficiency, a slight decrease in chromium uptake into the leather suggests that diffusion limitations may arise at very low water levels. Therefore, it can be concluded that high exhaustion tanning systems operating with 60% float offer a promising pathway toward water-saving leather production without sacrificing quality or environmental performance.

#### 4. CONCLUSIONS

This study demonstrates that substantial environmental and technical benefits can be achieved in chrome tanning through the implementation of a high exhaustion tanning system with reduced water usage. By lowering the float ratio to 60% and optimizing process conditions, it was possible to not only increase chromium uptake in leather but also significantly reduce residual chromium concentration in wastewater without compromising shrinkage temperature or overall leather quality. Compared to the conventional system, the high exhaustion approach resulted in up to 46% higher Cr<sub>2</sub>O<sub>3</sub> fixation in leather and a drastic reduction in effluent chromium levels, conductivity, and salinity. These improvements contribute directly to mitigating the ecological impact of tanning operations, particularly in terms of chromium discharge and salt pollution, which are among the industry's most pressing sustainability challenges. The findings confirm that reducing water usage does not inherently diminish tanning efficiency; rather, when appropriately engineered, it enhances exhaustion performance. Among the tested float levels, the 60% water ratio emerged as the optimal condition, offering the best balance between environmental performance and leather properties.

In conclusion, this study offers a viable and practical solution for the leather industry to advance toward cleaner production practices. The proposed high exhaustion tanning methodology enables significant reductions in both water consumption and chemical discharge, paving the way for more sustainable chrome tanning without sacrificing product performance thus making it suitable for broader industrial application.

#### REFERENCES

[1] J. Hu, Z. Xiao, R. Zhou, W. Deng, M. Wang, and S. Ma, "*Ecological utilization of leather tannery waste with circular economy model*", Journal of Cleaner Production, vol. 19, pp. 221-228, 2011.

[2] E. Önem, H. A. Karavana, A. Yorgancıoğlu, and B. Başaran, "Deri sanayinde ihracatı tehdit eden yasaklı maddelerin ayakkabılık mamul derilerde araştırılması", DEÜ Mühendislik Fakültesi Fen ve Mühendislik Dergisi, vol. 19, pp. 410-420, 2017.

[3] UNIDO, Registration, evaluation, authorisation and restriction of chemicals (REACH), Review of EU normative documents and legislation and their relevance for the tanning industry in developing countries, 46p, 2010.

[4] The European Green Deal Commission, Communication from the Commission to the European Parliament, The European Council, The Council, The European Economic and Social Committee and the Committee of the Regions, Brussels, 11.12.2019.



[5] R. A. Palop and A. Marsal, "Factors influencing the waterproofing behaviour of retanning-fatliquoring polymers-Part I", Journal of the American Leather Chemists Association, vol. 99, pp. 409-415, 2004.

[6] P. Thanikaivelan, S. Silambarasan, R. Aravindhan, and J. R. Rao, "*Non-polar medium enables efficient chrome tanning*", Journal of the American Leather Chemists Association, vol. 112, pp. 338-346, 2017.

[7] C. Zhang, F. Xia, B. Peng, Q. Shi, D. Cheung, and Y. B. Ye, "Minimization of chromium discharge in leather processing by using methanesulfonic acid: A cleaner pickling-masking-chrome tanning system", Journal of the American Leather Chemists Association, vol. 111, pp. 435-446, 2016.

[8] M. Prokein, M. Renner, and E. Weidner, "*Fast high-pressure tanning of animal skins by accelerated chromium sulphate complexation*", Clean Technologies and Environmental Policy, vol. 22, pp. 1133-1143, 2020.

[9] M. Prokein, M. Renner, E. Weidner, and T. Heinen, "Low-chromium- and low-sulphate emission leather tanning intensified by compressed carbon dioxide", Clean Technologies and Environmental Policy, vol. 19, pp. 2455-2465, 2017.

[10] C. R. China, M. M. Maguta, S. S. Nyandoro, A. Hilonga, S. V. Kanth, and K. N. Njau, "Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review", Chemosphere, vol. 254, pp. 126804, 2020.

[11] Y. Dilek, B. Basaran, A. Sancakli, B. O. Bitlisli, and A. Yorgancioglu, "*Evaluation of collagen hydrolysate on the performance properties of different wet-white tanned leathers*", Journal of the Society of Leather Technologists and Chemists, vol. 103, pp. 129-134, 2019.

[12] O. Yilmaz, H. Ozgunay, E. Onem, B. Basaran, A. Yorgancioglu, "*Trials on Synthesis of Syntans from Various Monomers and Determination of Their Tanning Performances*", Annals of the University of Oradea-Fascicle of Textiles, Leatherwork, vol. 23, pp. 101-108, 2022.

[13] A. Azhar, I. A. Shaikh, N. A. Abbasi, N. Firdous, and M. N. Ashraf, "Enhancing water efficiency and wastewater treatment using sustainable technologies: A laboratory and pilot study for adhesive and leather chemicals production", Journal of Water Process Engineering vol. 36: pp. 101308, 2020.

[14] P. M. Aquim, E. Hansen, and M. Gutterres, "*Water reuse: An alternative to minimize the environmental impact on the leather industry*", Journal of Environmental Management, vol. 230, pp. 456-463, 2019.