Zeolite tanning agent - sustainability considerations

Francina Izquierdo[1], Ivo Reetz[2], Anna Bacardit[3]

1 Pulcra Chemicals SL, Polígono San Vicente, s/n, 08755 Castellbisbal, Spain, info@pulcrachem.com

2 Pulcra Chemicals GmbH, Isardamm 79-83, 82538 Geretsried, Germany, info@pulcrachem.com

3 Universitat de Lleida, Av. Pla de La Massa, 8, 08700 Igualada, Spain

ABSTRACT

Zeolites are valuable pretanning agents that enhance the performance and quality of leather. By introducing masking agents and hydrotropic substances, the usage properties of the leather are significantly improved, particularly in terms of softness and a round, supple handle. The biodegradability of the pretanned/tanned leathers was assessed using ISO 20136, revealing a 94% degradation rate compared to non-tanned collagen—considerably higher than that achieved with conventional tanning methods. Additionally, compostability, as measured according to ISO 20200, was found to be high, further reinforcing the environmental benefits of this approach. In this context, the role of vegetable tanning agents used in conjunction with the zeolite system is explored, as they have a substantial influence on the compostability of the resulting leather.

Furthermore, a life cycle assessment (LCA) indicates that this novel tanning method offers notable environmental advantages over traditional processes, particularly chrome tanning. Finally, the advantages and potential drawbacks of this innovative combined tanning method are discussed, providing a comprehensive evaluation of its sustainability and practical applications.

Keywords: zeolite tanning, biodegradability, compostability, chrome-free leather, vegetable tannins, sustainable leather processing

1. Introduction

The shift toward more sustainable leather processing has led to growing interest in chrome-free tanning systems. Zeolite-based complex tanning preparations represent a promising alternative due to their mineral origin, environmental safety, and good leather properties. These hybrid systems combine the functional benefits of inorganic and bio-based substances to enhance the properties of the final leather while ensuring minimal environmental impact.

This paper examines the environmental performance and practical implications of complex zeolite-based tanning systems, with a focus on biodegradability and compostability. Results are based on standardized testing procedures including ISO 20136 (biodegradation) and ISO 20200 (compostability).

Finally, Life Cycle Assessment (LCA) is known for providing detailed information on various types of environmental impacts and is used in this study to compare a zeolite preparation with other tanning agents. Among the impact categories, climate change - expressed as Global Warming Potential (GWP) is considered the most fundamental outcome of the LCA.

2. Materials and Methods

2.1. Products tested

In this study, 3 commercial zeolite preparations of Pulcra Chemicals were used.

- **ZP1** and **ZP2** are zeolite preparations with a zeolite content of 30%. They further contain masking agents and a bio-based polymers for enhancing performance in application.
- **ZP3** is a masked zeolite with a zeolite content of 91%.

Phenolic, acrylic, naphthalene sulfonic and proteinic auxiliaries used in some of the trials are all commercially available products of Pulcra Chemicals. Chromium sulphate 33% Basicity (Cr-Sulf), tara and mimosa were obtained from a tannery supplier.

2.2. Test of Biodegradability

Biodegradability was assessed with pretanned/tanned leathers, which were obtained by the treatment of bovine split pelts of 2.8-3.0 mm with various tanning agents at a pickle pH of 2.3. In the case of zeolite use, the amount of tanning agent was adjusted so as to have 2.7-3.0 % of zeolite based on pelt weight. Tanning was run overnight, followed by a basification to pH 4.8 the next day. Chrome tannage with 8% of Cr-Sulf was done for comparison. The shrinkage temperature of the pretanned/tanned leather was determined. Biodegradability was measured according to **ISO 20136** – *Leather – Determination of degradability by microorganisms* at INESCOP at Elda-Alicante in Spain.

2.3. Test Compostability

2.3.1. Sample denomination

Seven types of leather were prepared for this study:
- Samples A–E: Zeolite-tanned (ZP1-3), combined with phenolic and vegetable agents (tara or mimosa)

Leather	A	B	C	D	E
Zeolite preparation	10% ZP1	10% ZP1	10% ZP1	10% ZP2	3% ZP3
Total Zeolite content	3.0%	3.0%	3.0%	3.0%	2.7%
Vegetable extract	20% Tara	20% Mimosa	-	-	-
Phenolic syntan	10%	10%	30%	30%	30%

Tab. 1. Products used for samples A-E

- Sample F: Tanned with 7% Cr-Sulf + 30% phenolic syntan
- Sample G: Wet blue, retanning with Cr-Sulf + 5% protein auxiliary, 5% acrylic resin and 1,5% naftalensulfonic acid.

All pretanned/tanned leathers were retanned and fatliquored with a standard recipe, which involved fatliquoring with synthetic and natural, anionic fatliquors.

All samples had thicknesses between 1.2 and 1.8 mm. They were subjected to standardized laboratory-scale composting according to **UNE-EN ISO 20200:2023** – *Plastics – Determination of the degree of disintegration under simulated composting conditions in a laboratory-scale test.*

2.3.2. Composting Setup

A synthetic solid waste matrix was prepared, containing sawdust, rabbit feed, mature compost, corn starch, sucrose, corn oil, and urea. Leather fragments were added to 1 kg of moist compost per box. Each reactor was kept at 58 °C for 60 days (thermophilic phase, Incubation #1). The non-composting samples were kept for another thermophilic incubation at 45°C for 30 days (Incubation #2), followed by a mesophilic incubation at 25 °C for another 84 days (Incubation #3).

2.3.3. Assessment Methods

Compostability was assessed following **ISO 20200**. The maturity of the compost was measured according to Rottegrade test. During the composting, pH, moisture, organic matter, total organic carbon, Total Kjeldahl was determined. At the end of composting, the amount of heavy metals (ISO 17072-2) was determined. Leachate characterization was done according to **UNE-EN 12457-4**: *Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges.* In particular, DQO, BOD_5, nitrogen, salts, and selected metals (Cr, Fe, Zn) were analyzed.

2.4. Life Cycle Assessment (LCA)

LCA analysis was performed at A3 Leather Innovation Center of the Universitat de Lleida according to **ISO 14040:2006** – *Environmental management – Life cycle assessment – Principles and framework*, using as a base 1000kg of the tanning agent. System boundaries were defined so as to follow a cradle-to-gate approach, including raw material extraction, transportation, energy and water consumption, waste generation, and emissions up to the point of product delivery at the factory gate. Ecoinvent 3.9.1 (December 2022) was used as database and the software was OpenLCA 2.4.1. Environmental Footprint (EF) 3.1 Midpoint indicators was the impact assessment indicator.

3. Results and Discussion

3.1. Biodegradability

The result of biodegradability of the pretanned/tanned leathers is displayed in the table below. In the method used, biodegradability is assessed in relation to untanned collagen. It is clear that all zeolite preparations show an extremely high biodegradability, which is over 15 times higher than with standard chromium tannage.

Product	**ZP1**	**ZP2**	**ZP3**	**Cr-Sulf**
% Tanning agent	10	10	3	7
Total % Zeolite	3	3	2.7	-
T_S, °C	75	78	60	>100
% rel. biodegradability	94.1	99.8	96.3	6.0

Tab. 2. Summary test biodegradability and measurement of shrinkage temperature

Zeolite-pretreated leathers surely exhibit high biodegradability due to the nature of the tanning process. Activated zeolites were found to form an aluminosilicate network structure covering the collagen fibers, which stabilizes the protein fiber structure (Wise et al. 2023). Thus, collagen fibers are primarily stabilized through physical encapsulation, rather than by chemical bonds. This interaction minimally inhibits microbial activity, allowing efficient enzymatic degradation.

In contrast, chrome tanning creates strong coordination complexes between chromium (III) ions and collagen functional groups. These chemical cross-links improve thermal and hydrolytic stability but reduce biodegradability by limiting microbial degradation.

Regarding shrinkage temperature, we observe a significant improvement with the bio-based components used in the formulation of the respective zeolite preparations (ZP1 and ZP2). In fact, full penetration and sufficient stabilization can be achieved without the use of syntans in the tanning process. In contrast, the masked zeolite results in a lower shrinkage temperature. Therefore, in this case, additional tanning auxiliaries such as phenolic syntans would be required to enhance leather quality. The use of material of natural origin also further increases the bio-based C content of the leather (Reetz 2023).

3.2. Disintegration and Compostability

Composting leather waste is an ecological solution aligned with circular economy principles, offering an alternative end-of-life route for leather products or tannery residues. It helps reduce the volume of waste generated by the leather industry, lowers waste management costs for tanneries, and produces nutrient-rich material that can be used to improve soil fertility.

Industrial composting is an aerobic process conducted under controlled conditions, with key factors such as temperature (50–60 °C), moisture, oxygen, particle size, and C/N ratio influencing its efficiency. Unlike home composting, industrial systems maintain higher temperatures, accelerating decomposition.

The process yields CO_2, water, and nutrient-rich compost suitable for agricultural use. It operates without chemicals and offers environmental benefits by reducing greenhouse gas emissions, replacing mineral fertilizers, and enhancing soil carbon storage (Sardroudi et al. 2024).

Out of the seven leather samples tested, five (A, C, D, E, G) were fully disintegrated within 10–37 days at 58 °C. Samples B (ZP1 + mimosa) and F (Cr-Sulf + phenolic syntan) showed incomplete degradation even after an additional 90-day mesophilic phase. All successfully composted materials met maturity criteria (Rottegrade grade V), indicating safe and stable composting. Interestingly, also in the case of the non-composting samples B and F, Rottegrade grade V was reached, indicating that the process of decomposition under the conditions applied would not further proceed.

The difference in degradation between Leathers A–C highlights the significant impact of vegetable tanning on compostability of the zeolite tanned leathers. While all tanning agents negatively affect the composting rate to some extent, **hydrolysable tannins**, such as tara (Leather A), still allow good compostability. Microorganisms can readily cleave the ester bonds between the saccharide moiety and the phenolic rings of hydrolysable tannins (Escabrós et al., 2023). This also appears to be the case for leathers tanned with zeolite.

In contrast, **non-hydrolysable tannins**, such as those in mimosa (Leather B), are much more resistant to degradation. Under the test conditions, practically no decomposition was observed. Therefore, when producing zeolite-tanned leathers intended for composting, the choice of vegetable tanning agents should be carefully considered.

Parameter	A	B	C	D	E	F	G	Blank (t=60d)	Blank (t=0)	Unit
Incubation	1	1-3	1	1	1	1-3	1	1	-	
Degradation time	28	-	14	10	14	-	37	-	-	days
Decomposition rate	100	0	100	100	100	0	100	-	-	%
Test Rottegrade	V	V	V	V	V	V	V	V	I	Grade
Organic Material	68	88	68	80	80	89	76	80		%
Total Organic Carbon	33	44	33	40	41	45	38	40		%
Kjeldhal Nitrogen	1.5	1.8	1.4	1.5	1.5	1.8	1.5	1.4		%
Relation C/N	23	24	24	27	28	25	26	29		%
Dry weight	47	44	49	46	47	52	40	36		%
Humidity	53	56	51	54	53	48	42	64		%
Ash content (550°C)	4.7	5.9	4.1	3.5	3.5	5.6	3.9	3.7		%
pH	7.7	7.8	7.8	7.8	7.7	7.6	7.8	7.9		
				Heavy metals						
Cd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		mg/kg
Cu	12.2	12.3	12.3	10.3	10.3	12.8	17.6	8.0		mg/kg
Zr	<12	<12	<12	<12	<12.0	<12	<12	<12		mg/kg
Cr	6.2	6.1	6.2	5.3	7.1	45.6	513	4.1		mg/kg
Zn	37	54	36	32	34	45	7	25		mg/kg

Fe	491	712	553	429	446	628	513	501	mg/kg
Ni	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	mg/kg
Pb	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	mg/kg

Tab. 3. Results of Compostability

Regarding the type of Zeolite preparation (Leathers C-E), there is no significant difference between the various zeolites used. Also, the use of the phenolic syntan in conjunction with zeolite seems to have a relatively low impact. At least, it is lower than the use of vegetable tanning agents (Leather C vs. A and B).

Chrome tanning is known to result in leather with relatively poor compostability (Escabrós et al., 2023). When chrome-tanned leather is retanned with a high amount of phenolic syntan, as in Leather F, it becomes non-compostable. However, when combined with other types of retanning agents—such as acrylic resins, naphthalene sulfonates, or protein hydrolysates—compostability remains within an acceptable range.

The higher nitrogen content in the samples containing leather pieces is directly a result of the deterioration of the collagen. All samples had suitable C/N ratios (23–29), ensuring optimal microbial activity.

Curiously, the humidity in the samples containing leather pieces was found to be lower than in the case of the pure compost—something that is often observed in composting trials with leather. A possible explanation for this phenomenon is the heat evolved during the decomposition of proteins. The slightly higher temperature leads to increased evaporation of water.

Regarding heavy metals, the chromium content in the compost from sample G, which originated from wet-blue leather, was relatively high. In fact, it would not meet the legal limits for compost as set by Real Decreto 506/2013 (Spain), which allows a maximum of 300 mg/kg of Cr for the lowest grade Class C compost. All other heavy metal concentrations in the compost samples were within the permissible limits specified by the regulation.

Leachate is the liquid that drains or "leaches" from composting material. It contains dissolved organic and inorganic substances released during the decomposition of organic matter. Assessing leachate quality is a key component of compost evaluation from the perspectives of environmental safety, regulatory compliance, and the assessment of compost quality and maturity.

Parameter	A	B	C	D	E	F	G	Blank (t=60d)	Unit
pH	7.8	7.4	7.8	8.2	8.0	8.1	8.1	8.2	
COD	2.8	1.8	2.7	3.1	2.5	2.0	3.2	2.8	g/L
BOD 5d	420	--	154	258	256	--	295	278	mg/L
Conductivity 25ºC	3.4	4.1	3.9	4.3	4.3	3.9	3.6	3.1	mS/cm
Total nitrogen	463	474	454	284	395	480	654	606	mg/L
Nitrogen-amonia	55	15	87	35	35	12	47	81	mg/L
Anions									
Cl^-	1.285	817	873	858	885	806	733	735	mg/L
SO_4^{2-}	1.316	971	1.096	1.262	946	589	663	1.190	mg/L
NO_3^-	<10	<10	<10	<10	<10	<10	<10	<10	mg/L
Heavy metals									
Ti	<12	<12	<12	<12	<12	<12	<12	<12	mg/L
Al	71.4	1.9	64.3	50.2	47.7	1.5	42.9	52.7	mg/L
Zr	<12	<12	<12	<12	<12	<12	<12	<12	mg/L
Cr	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	13.5	<3.0	mg/L
Zn	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	mg/L
Fe	22.5	<3.0	23.6	18.1	19.2	<3.0	22.3	21.8	mg/L

Tab. 4. Analytic results for the leachate

Leachates exhibited a neutral to slightly alkaline pH (7.4–8.2). DQO and BOD_5 values were moderate, and no significant accumulation of harmful substances was detected, confirming environmental safety. Thus, in all cases, the tanned leather samples demonstrated favorable results in terms of leachate quality.

3.3. Life cycle assessment (LCA)

The Life Cycle Assessment (LCA) for Global Warming Potential (GWP) revealed that the zeolite product ZP1 performs significantly better than both chrome-based tanning agents and conventionally manufactured zeolite A. Synthetic alternatives such as glutaraldehyde and phenolic syntans show particularly low CO_2-equivalent emissions, basically due to the high efficiency of large-scale, energy-optimized industrial production. In contrast, bio-based materials tend to have higher GWP values, primarily due to emissions related to land use. GWP is considered a key indicator because of its critical relevance to global sustainability.

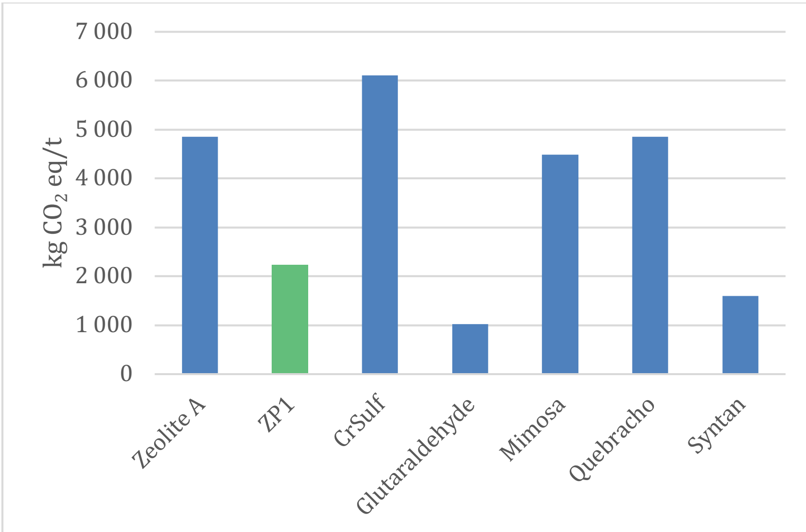

Fig. 1. GWP 100 results for different tanning agents

4. Conclusions

Zeolite-based tanning systems offer a sustainable and high-performance alternative to conventional chrome tanning. Compared to chrome-tanned leather, zeolite-tanned leathers demonstrate significantly improved biodegradability and compostability. However, special attention must be given to the choice of vegetable tanning agents - only hydrolyzable vegetable tannins are suitable for producing compostable leather. In contrast, synthetic tanning agents used in combination with zeolite show minimal influence on compostability.

The absence of toxic residues and heavy metals further strengthens the case for zeolites in environmentally conscious leather production. Additionally, the low Global Warming Potential (GWP) observed in the Life Cycle Assessment (LCA) confirms that zeolite-based tanning is highly favorable from a sustainability perspective.

5. Acknowledgements

We would like to thank ACCIÓ for financing the project “CUPONS GREEN”, and the Universitat de Lleida for the collaboration in this work.

6. References

Escabrós, J., Autenrieth, B., Koch, R., Barenys, J., A truly versatile material: insights on the compostability and the biodegradability of leather, World Leather, 36 (6), 18-23, 2023

Reetz, I., Bio-based chemicals for leather processing, World Leather, 36 (1), 30-31, 2023

Sardroudi, N., Sorolla, S., Casas, C., Bacardit, A., A Study of the Composting Capacity of Different Kinds of Leathers, Leatherette and Alternative Materials, Sustainability, 16, 2324, 2024

Wise, W.R., Davis, S.J., Hendriksen, W.E., van Behr, D.J.A., Prabakar, S, Zhang, Y., Zeolites as sustainable alternatives to traditional tanning chemistries, Green Chem., 25, 4260–4270, 2023