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Life cycle assessment insights into nanosilicates-based chrome-free tanning processing towards eco-friendly leather manufacture

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ABSTRACT

Chrome tanning system has been faced with great challenges from potential environmental and human health risks and environmental pressures in the leather industry. The development of chrome-free tanning system towards eco-friendly leather manufacture is the main strategy to solve them from the source. However, appropriate assessments of the physical and environmental properties of a new tanning process remain challenging. In this work, we compared the physical performances and environmental impacts of two nanosilicates-based chrome-free combination tanning systems with conventional chrome tanning system in practical fur leather processing. The objective of this study was to obtain comprehensive insights into the nanosilicates-based chrome-free combination tanning systems from both technical and environmental perspectives. All fur leathers possessed similar and integrated fleece structures, ensuring high glossy and flexibility of final fur leather articles. Tara tannin-Zeolite (TA-ZE) combination tanning system was chosen as the most promising one for manufacturing garment leather articles. The resultant leathers were endowed with favorable physical properties (e.g., tear strength of 15.9 N, elongation at break of 42.3%, shrinkage temperature of 98.6 °C) and no restricted Cr(VI) and free formaldehyde. Life cycle assessment (LCA) results revealed that the TA-ZE combination tanning system exhibited better environmental impacts than other options. The main novelties included the contribution to avoiding the use of high-risk tanning chemicals by presenting a better technical and environmental alternative in the leather processing and the application of LCA to environmentally evaluate the leather processing. We envision these findings can offer comprehensive insights into emergent chrome-free combination tanning systems for designing and rationalizing feasible fur leather processing towards eco-friendly leather manufacture.

1. Introduction

The manufacture of leathers involves a series of suitable chemical and physical processes aiming to convert the collagen fibers of hides or skins into the leathers with the characteristics required for the intended purposes (Covington and Wise, 2020). Currently, there are growing global demands for novel eco-friendly leather articles owing to their excellent biodegradability, preferable ecological benefits, and desirable waste minimization (Covington and Wise, 2020; Grinberga-Zalite and Zvirbule, 2022; Nworie et al., 2022; Ratnawati et al., 2022). Unfortunately, conventional leather processing based on typical leather chemicals with very high concern, such as chromium and free formaldehyde, has always been faced with great challenges from potential environmental and human health risks and environmental pressures in the global leather industry (Ding et al., 2018a; Gao et al., 2022; Jia et al., 2019). Therefore, avoiding the utilization of these high-risk leather chemicals to develop novel eco-friendly leather manufacture has become one of the main concerns in the leather industry during the last decades.

Currently, the combination systems of chromium-aluminum and formaldehyde-aluminum are the two frequently used tanning systems in the conventional fur leather processing (Ding et al., 2018b). The former can generate the leathers with high thermal stability, favorable softness, and fullness, and the resultant surface positive charges of leathers are

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suitable for subsequent post-tanning procedures (Ding et al., 2015). However, some leather chemicals used in the post-tanning procedures can lead to possible conversions of Cr(III) to Cr(VI), which can cause severe allergic contact dermatitis in human skin even at very low concentrations (Fontaine et al., 2019; Hedberg, 2020; Hedberg et al., 2014). The latter can afford the leathers with a white appearance, pleasant softness, alkali, and oxidative resistance, and free formaldehyde can be sustainably released during the post-tanning processing and the usage of fur leather articles (Li et al., 2008). The restrictions on the amount of free formaldehyde in the leather articles, especially those in direct contact with skin, have become more stringent with increasing awareness of eco-labeling concepts among global customers and growing tendency of re-evaluating its potential risks to the human health (Kim et al., 2011). Hence, it is urgent to develop more environmentally friendly leather chemicals and the relevant processing technologies to reduce or to eliminate the environmental and human health risks of conventional fur leather processing from the source. These feasible strategies can meet the current requirements of global consumers for versatile eco-leather products (Ding et al., 2020; Hao et al., 2020; Jiang et al., 2021).

More recently, the chrome-free combination tanning systems by using natural vegetable tannins (Ahmed et al., 2022; China et al., 2020; Xiao et al., 2023), aldehydes (Gao et al., 2019; Wang et al., 2023), and other biomass-derived tanning agents (Ding et al., 2022, 2023; Hao et al., 2023; Liang et al., 2023), towards eco-friendly leather manufacture have been emphasized in order to reduce the environmental and human health risks of conventional leather processing. In our recent studies, the combination tanning systems based on nanosilicates with tuneable surface properties, large surface area, and excellent biocompatibility (Serrano et al., 2013; Tomás et al., 2018) with tetrakis (hydroxymethyl) phosphonium salts (Shi et al., 2019), and hydrolyzable vegetable tannins (Shi et al., 2021), have been developed as feasible chrome-free tanning approaches with appropriate tanning properties. It could be mainly owing to the fact that these nanosilicates can be controllably diffused into the collagen microstructures, especially the collagen fibrils, stabilizing the intrinsic triple-helical conformation of collagens, which can act as nano-tanning agents (Shi et al., 2018, 2024). The fixation of nanosilicates with the collagens not only enhances the tanning properties of the resulting leathers, but also endows the leathers with improved yellowing resistance and lightfastness. Nevertheless, the potential environmental impacts of these combination tanning systems have not been involved so far, especially in the fur leather processing (Baquero et al., 2021; Esquerra-Resa et al., 2022; Sivakumar, 2022). Actually, more comprehensive environmental assessments of a new tanning process related to the potential human health and environmental risks are essential for further promoting chrome-free combination tanning systems towards eco-friendly leather manufacture. But appropriate assessments of a new tanning process from both technical and environmental perspectives remain challenging (Marrucci et al., 2022; Navarro et al., 2020; Yu et al., 2021).

In this work, we compared the fixation of two nanosilicates with skin collagen fibers and the environmental impacts of nanosilicates-based chrome-free combination tanning systems in rabbit fur leather manufacture. These processes were carefully checked from the perspective of physical performance evaluation, combined with the life cycle assessment (LCA) towards eco-friendly leather manufacture. We mainly focused on the enhancement of the nanosilicates to the physical performances of resultant fur leathers, the effects on the fleece structures of fur leathers, and the environmental impact assessment of fur leather processing from a life cycle perspective. Our objective was to obtain comprehensive insights into the nanosilicates-based chrome-free combination tanning systems from both technical and environmental perspectives.

2. Materials and methods

2.1. Materials

1000 kg rabbit skins were used as raw materials for the fur leather manufacture, which were provided by a tannery in Sichuan Dehua Leather Co., Ltd. in Sichuan province of China. The chemicals used for the processing were all in commercial grade, mainly concerning their excellent properties, wide applicability, and acceptable costs. Commercial chromium powder (Tankrom AB) and potassium aluminum ($KAl(SO_4)_2$) were bought from Sisecam Chemical Co. (Turkey) and BASF Chemical Co. (Germany), respectively. Tara tannin was purchased from Clariant Chemical Company (Switzerland). Zeolite (Teknotan G, aluminosilicate) was provided by Teknoleather Chemical Co. (Italy). Tetrakis(hydroxymethyl) phosphonium sulfate (THPS) (75%, w/w) was purchased from Xiya Chemical Industry Co., Ltd (China). Commercial Laponite RDS (LA), a synthetic nanosilicate modified with sodium pyrophosphate ($Na_4P_2O_7$), was purchased from BYK Additives & Instruments (U.K.). Other leather chemicals were commercial ones, which were purchased from Fanbo Chemical Co. (China).

2.2. Fur processing methods

In the fur leather manufacture, the chemicals were presented for three compared tanning methods. These combination tanning systems included Method I (chromium-aluminum, denoted as Cr–Al), Method II (tetrakis(hydroxymethyl)phosphonium sulfate-Laponite, denoted as THPS-LA), and Method III (Tara tannin-Zeolite, denoted as TA-ZE). Method I was a conventional tanning system as a control based on the previously reported method (Zhang and Wang, 2019). In Method II, THPS, one of typical commercial water-soluble quaternary phosphonium salts, was used. Specifically, active hydroxymethyl groups of THPS molecules can react with functional amino groups of collagen molecules through aldehydic reactions, thus conferring the resultant leathers with fine hydrothermal stability and enhanced fixation of anionic post-tanning chemicals. Moreover, positive THP^+ with low toxicity and no potential bioaccumulation can create ionic binding interactions with negatively surface-charged nanosilicates. It can form synergistic interactions between the THPS-modified nanosilicates and the collagen fibers in the formation of the leather matrix with reduced free formaldehyde release and improved physical properties (Shi et al., 2019). Therefore, THPS has been deemed as an effective chrome-free tanning agent. In Method III, hydrolyzable vegetable tannin, Tara tannin, in combination with aluminosilicate, commercial Zeolite, was applied for a chrome-free tanning system via synergistic interactions (e.g., hydrogen bonding and electrostatic interactions, and strong coordinated silicate-Tara networks crosslinked between the collagens). The resultant leathers exhibited pleasant pastel color and favorable lightfastness without containing any restricted substances (Shi et al., 2021).

The dosage was valuated over 20,000 L of water used, and the tanning phase included the pickling, tanning, and post-tanning operations. Table 1 listed Method I as the control to compare the new recipes with the conventional one. Tables 2 and 3 gave the optimized rabbit fur leather process recipe as per previously reported methods (Shi et al., 2019, 2021).

2.3. Determination of shrinkage temperature

The shrinkage temperature (T_s), a measure of hydrothermal stability of crust leathers, was determined by a shrinkage tester using the official method (ASTM, 2004). A 10 mm × 60 mm specimen was cut out from the leather sample and was inserted into the bath of water. Then, the tub was heated at a rate such that the rise in the temperature was kept at 2 °C per minute. The temperature at the first definite sign of the shrinking was recorded. The experimental plot was obtained from the average of three samples.

Table 1
Process recipe for fur leather by Method I: conventional Cr–Al combination system.

Procedures	Dosage	Chemicals	Time	pH	Remarks
Pickling	0.1 g/L	Bating enzyme			
	1 g/L	Defatting agent			
	2 g/L	HCOOH	30 min	3.0	
	1 g/L	Lactic acid			
Tanning	60 g/L	NaCl			25 °C
	10 g/L	Chrome powder			
	25 g/L	$KAl(SO_4)_2$	2 h		32 °C
	0.5 g/L	$NaHCO_3$	30 min	~4.5	Overnight
	2 g/L	Fatliquoring agent	30 min		
Dyeing	40 g/L	NaCl			55 °C
	1 g/L	Leveling agent	30 min		
	4 g/L	Dyestuff	6 h		
	0.5 g/L	HCOOH	30 min	3.2	Drain

Table 2
Process recipe for fur leather by Method II: THPS-LA combination system.

Procedures	Dosage	Chemicals	Time	pH	Remarks
Pickling	0.1 g/L	Bating enzyme			
	1 g/L	Defatting agent			
	2 g/L	HCOOH	30 min	~3.5	
	1 g/L	Lactic acid			
	15 g/L	$NaHCO_3$	30 min	4.0	
Tanning	60 g/L	NaCl			25 °C
	1 g/L	Fatliquoring agent			
	6 g/L	THPS	3 h		
	1 g/L	LA	2 h		32 °C
	0.5 g/L	HCOOH	30 min	~3.5	Overnight
	1 g/L	Fatliquoring agent	30 min		
Dyeing	40 g/L	NaCl			55 °C
	1 g/L	Leveling agent	30 min		
	4 g/L	Dyestuff	6 h		
	0.5 g/L	HCOOH	30 min	3.2	Drain

Table 3
Process recipe for fur leather by Method III: TA-ZE combination system.

Procedures	Dosage	Chemicals	Time	pH	Remarks
Pickling	0.1 g/L	Bating enzyme			
	1 g/L	Defatting agent			
	2 g/L	HCOOH	30 min	~3.5	
	1 g/L	Lactic acid			
	15 g/L	$NaHCO_3$	30 min	4.0	
Tanning	60 g/L	NaCl			25 °C
	1 g/L	Fatliquoring agent			
	6 g/L	TA	3 h		
	1 g/L	Teknotan G	2 h		32 °C
	0.5 mL/L	HCOOH	30 min	~3.5	Overnight
	1 g/L	Fatliquoring agent	30 min		
Dyeing	40 g/L	NaCl			55 °C
	1 g/L	Leveling agent	30 min		
	4 g/L	Dyestuff	6 h		
	0.5 g/L	HCOOH	30 min	3.2	Drain

2.4. Determination of the uptake of post-tanning chemicals

The uptake of dyestuffs by fur leathers was determined by total organic carbon (TOC) analysis. 1 mL floats were diluted to 100 mL with deionized water. The measurements were conducted on a TOC/TNb analyzer (LiquiTOC/TNb, Elementar, Germany) coupled with an automatic sampler. The uptake of dyestuffs was expressed as the TOC reduction in the combination tanning processes, and calculated as per the following formula (1):

$$\text{Uptake} = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

where the C_t and C_0 were the concentrations of post-tanning chemicals expressed as the TOC values in the floats after and before the post-tanning procedures, respectively. Each plot was acquired from the average of three parallel experiments.

2.5. SEM-EDX analysis

The samples were taken from the grain, middle, and flesh layers of the crust fur leathers, respectively. After lyophilized at −43 °C in a freeze dryer (Alpha 1–2 LD, Christ, Germany) for 24 h, the samples were cut into the specimens with a thickness of 1.0 mm by a microtome (CM1900, Leica, Germany) before the observations. The morphologies of the leather specimens were recorded by a scanning electron microscope (JSM-7500F, JEOL, Japan) at an accelerating voltage of 15 kV. The relative elemental compositions of the specimens were confirmed by a coupled energy-dispersive X-ray spectroscopy (EDX) detector.

2.6. Physical performances and restricted hazardous substances measurements

The physical performances of fur leathers regulated by the current standard requirements for fur garment leather articles (QB/T 2822-2018) were measured according to the official standards (QB/T1269-2012). Moreover, the contents of Cr(VI) and free formaldehyde (HCHO), the two restricted hazardous substances in the leathers, were measured with IUC 18-2 and IUC 19-2, respectively, compared to the latest Eco-label criteria (2009/563/EC) for the footwear of European Union (EU). Each plot was collected from the average of three parallel experiments.

2.7. Methodology used for environmental impacts assessment

The life cycle assessment (LCA) methodology using the standard ISO 14040–14044 (2006) was applied to quantitatively evaluate the environmental impacts of the two chromium-free tanning processes (Method II and Method III), compared with the conventional chrome-aluminum one (Method I). The system boundaries of these methods to be compared, as well as their foreground inventory data, were presented in Fig. 1 (Method I: Cr–Al), Fig. 2 (Method II: THPS-LA), and Fig. 3 (Method III: TA-ZE). The LCA study was performed from the skins, which were arrived at the tannery, to the finished fur leathers, which were left from the company, (e.g., from gate to gate). The functional unit was 1000 kg of rabbit skins, which were arrived directly from the slaughterhouses, and were processed with these three different methods. The differences among the three methods to be compared were mainly in the tanning steps. All previous processing steps (soaking, swelling, and defatting) were the same, as well as the dyeing. In the case of pickling, it was an important step to prepare the system for tanning, so it varied with tanning method that would be used. The tanning step was completely different among these methods, with different specific chemicals that also affected the wastewater pollutants content. Hence, the main characteristics of the pickling/tanning/dyeing effluents were analyzed as shown in Figs. 1–3, and there were the differences in the COD, TSS, TN, TOC, and Cr content (the last one present only in the Method I wastewater). Considering these differences, the wastewater treatment (WWT) was also included in the systems to be compared.

In every process step, the same weight change of rabbit skins was considered by following the relative European documentation. This procedure didn't affect the final environmental impacts but was important to achieve a more realistic model. The Leather PEF category rules were followed as much as possible (especially for the modeling of chemicals), although it had to be mentioned that these rules were written only considering hides, sheep, or goat skin tanning. The tanning in this study was related to the rabbit furs. The study was modelled using GaBi software 2023 (LCA for Experts 10.7.0.183), and the database used was Ecoinvent 3.8 and Sphera. The impact categories were the ones from the EF 3.0 methodology.

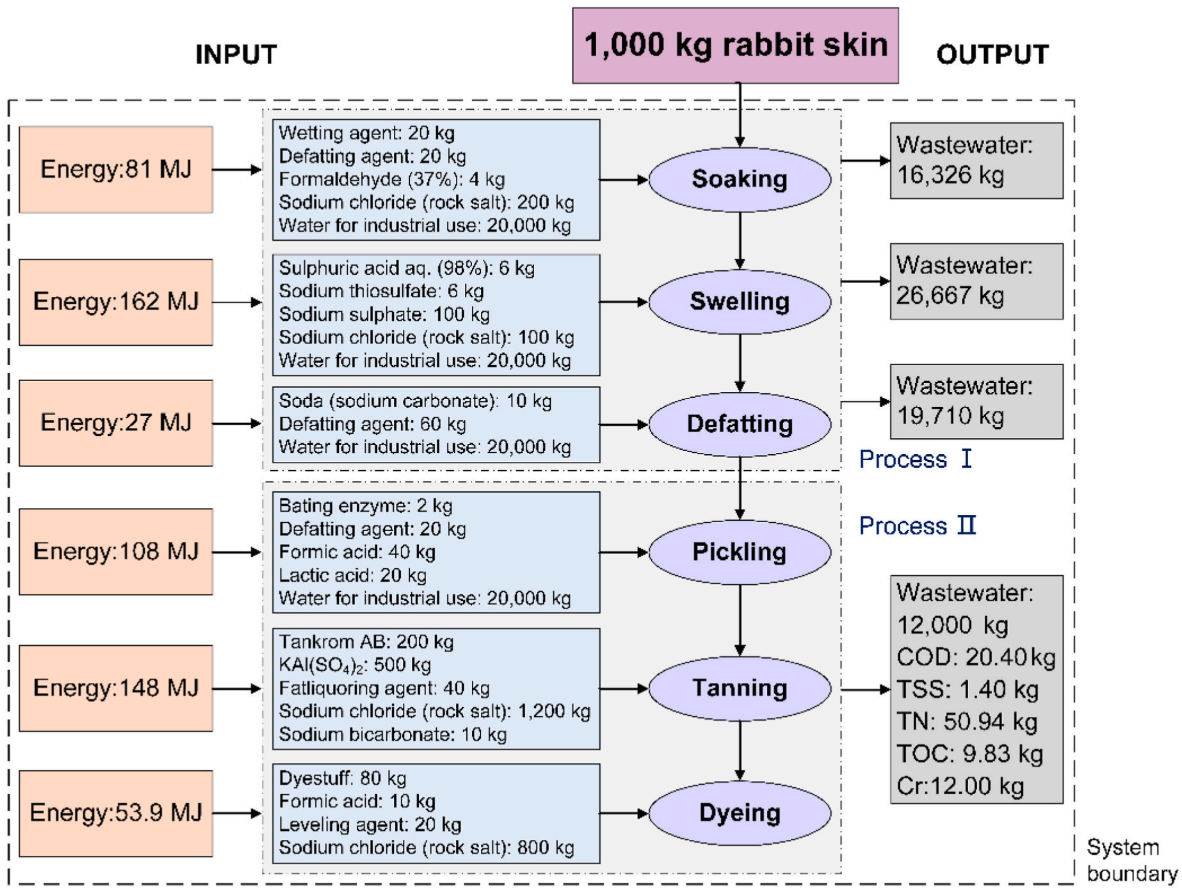

Fig. 1. Flow sheet of chemicals and energy inventory for conventional process, Method I (Cr–Al), in rabbit fur leather manufacture (COD: Chemical Oxygen Demand; TSS: Total Suspended Solid; TOC: Total Organic Carbon; TN: Total Nitrogen).

As shown in Figs. 1–3, the process was divided into two main steps: Process I (soaking, swelling, and defatting) and Process II (pickling, tanning, and dyeing). The differences in the inputs and outputs among the methods were only in Process II. Therefore, Process I was not important for the comparison, but it was included for a complete study of the whole tanning process. The main differences between the three compared methods were the type of chemicals used during the processing steps as well as the number of pollutants in the wastewater.

For the WWT, two different process units from the databases were used, one for "Process I″ and the other for "Process II". For "Process I″, an average global municipal wastewater treatment process was used, while in the case of "Process II" (to be able to better model the differences in the number of specific pollutants), a parametrized WWT process was needed. In this way, the process permitted to specify the amount of every pollutant entering the WWT for each method.

The modeling of the chemicals and substances in the software was performed according to the Product Environmental Footprint Category Rules (PEFCR) guidelines for the leathers, and the chemicals were modelled according to the scientific knowledge with the best "proxy" substances available.

The selection criteria for every process were in line with the aim of modeling the systems as accurately as possible for the case of Chinese production. Therefore, the processes were chosen above averages and global or rest of the world processes above other options (like European or United States).

In the case of Tara tannin, it was an extract derived from fruits of Tara trees (Caesalpina spinosa), native to South America. It wasn't possible to use a similar process unit due to the lack of data in the Ecoinvent database about this fruit and the extraction of Tara tannin from it (Kılıç et al., 2023). Hence, it was modelled from the reported impacts of a "proxy substance", and natural tannins extracted from the chestnut production process were found in the OpenLCA 1.11. Data came from Life Cycle Data Network and a previous version of the Ecoinvent v3.3 database, according to the leather PEFCR. Hence, although the tannin extraction process was not available in the current Ecoinvent databases, it was modelled in this study, considering impacts reported before and recommended in the leather PEFCR. There were still some unsolved issues about this modeling, such as the zero impact in the water use and climate change impact categories, whose reasons were not explained in the database and the related documents.

The energy consumption (heating and mechanical energy) was modelled as the electricity for a better reproduction of the lab-scale operating conditions, where three methods were tested. A general Chinese electricity supply mix, the SGCC (State Grid Corporation of China) low voltage, was also chosen (Rikap, 2022).

3. Results and discussions

3.1. Effects of combination tanning systems on the physical performances of rabbit Fur leathers

Fig. 4a showed the shrinkage temperature (T_s) of rabbit fur leathers which were manufactured by the combination tanning systems. It should be noted that the fur leathers tanned by Cr–Al, THPS-LA, and TA-ZE combination tanning systems exhibited the T_s of 89.1 °C, 82.6 °C, and 98.6 °C, respectively. It was understandable that the synergistic interactions of nanosilicates with Tara tannin, such as coordinated silicate-Tara networks between the collagen molecules, were much stronger than those of tetrakis(hydroxymethyl) phosphonium salts, such as hydrogen and ionic bonds (Shi et al., 2018, 2019, 2021). Moreover, as

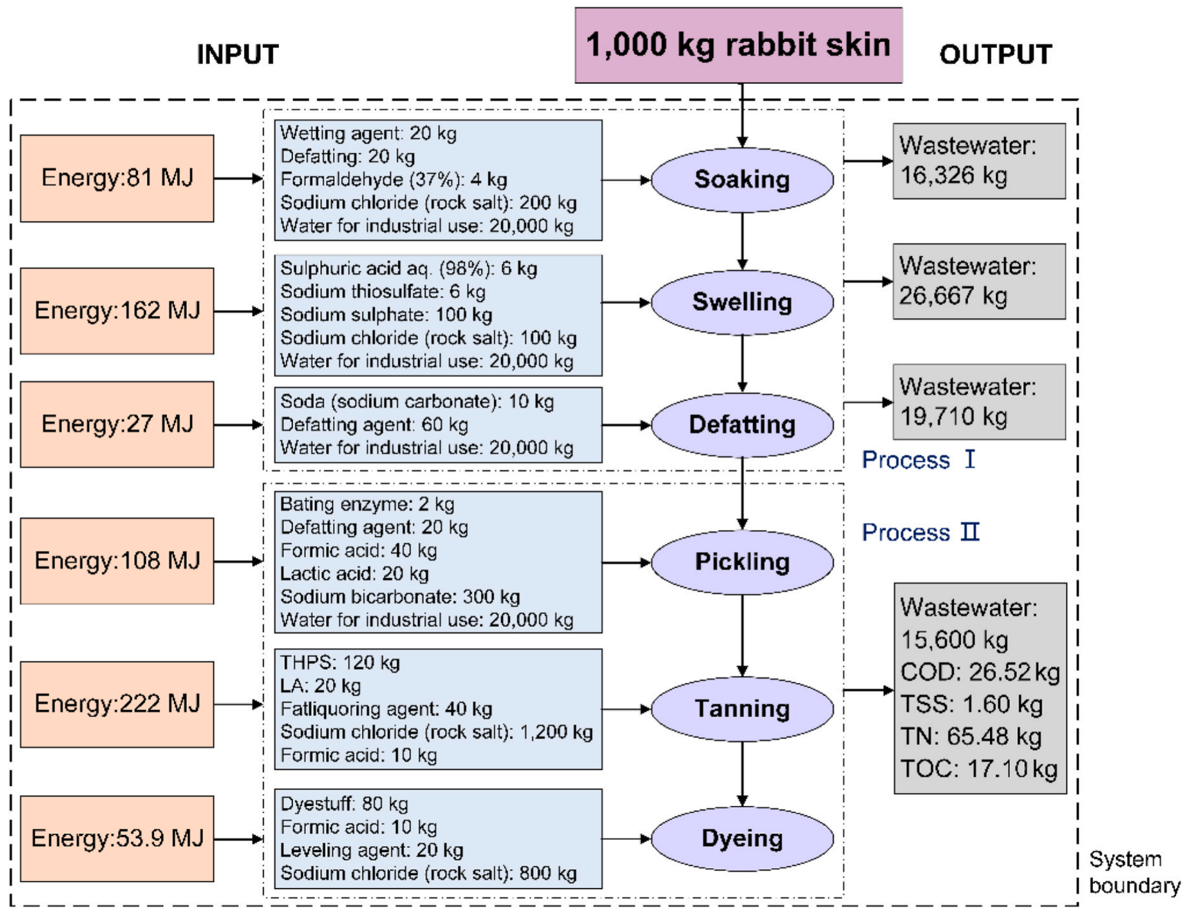

Fig. 2. Flow sheet of chemicals and energy inventory for Method II (THPS-LA) in rabbit fur leather manufacture (COD: Chemical Oxygen Demand; TSS: Total Suspended Solid; TOC: Total Organic Carbon; TN: Total Nitrogen).

given in Fig. 4b, the corresponding dyestuff uptake by the leathers was calculated as 96.8%, 98.2%, and 96.1%, respectively. It implied that each of these chrome-free combination tanning systems had comparable dyeing properties with the Cr–Al tanning system. More importantly, it can be clearly seen from Fig. 4c–h that all the resultant fur leathers possessed similar and integrated fleece structures in the combination tanning processes. This was desirable because the fleece structures of fur leathers could affect the gloss and strengths of the final fur leather articles (Zakharkevich et al., 2023). Further EDX line results in Fig. 5, which were obtained by scanning the cross section from the flesh to the grain side of the leather matrix, showed decreasing trends in the characteristic elements from these chrome-free combination tanning systems. This can be mainly due to the difference among the histological structures of collagen fibers exhibiting relatively non-uniform penetration of these tanning agents into the leather matrix (Yang et al., 2022).

3.2. Physical performances and hazardous substances measurements of rabbit Fur leathers

Proper physical performances of the leathers were prerequisite to ensure the comfort and safety of final leather articles (Zhang et al., 2004). Fig. 6 depicted the testing results of the physical performances (e.g., tear strength, elongation at break, T_s, and pH values) and hazardous substance (free HCHO) content in the rabbit fur leathers tanned by Cr–Al, THPS-LA, and TA-ZE combination tanning systems, respectively. It should be noted that these performances accorded with the specified values in the norms of current standard requirements for fur garment leathers (QB/T 2822-2018). Among them, the TA-ZE combination tanning system had better physical performances (namely, tear strength: 15.9 N; elongation at break: 42.3%; T_s: 98.6 °C; pH 3.5) than other combination tanning systems. More importantly, no restricted hazardous substances, e.g., Cr(VI) and free HCHO, were detected in the TA-ZE combination tanning system. Hence, it could showcase great promise for manufacturing fur garment leathers with high safety.

3.3. Life cycle assessment of rabbit Fur leather processing

The comparison of rabbit fur leather processing based on the Cr–Al, THPS-LA, and TA-ZE combination tanning systems, respectively, was performed considering the 19 impact categories recommended on the Method EF 3.0 (European Commission, 2023). The Method EF 3.0 contained the set of more relevant impact categories to obtain the environmental profiles of a product and the best method to evaluate each of them. These impact categories included: Acidification (AC, mole of H^+ equivalent), Climate change – Total (CC – Total, kg CO_2 equivalent), Climate change biogenic (CC – biogenic, kg CO_2 equivalent), Climate change fossil (CC – fossil, kg CO_2 equivalent), Climate change land use and land use change (CC – LUC, kg CO_2 equivalent), Ecotoxicity freshwater total (Ecotox Water – Total, Comparative toxic unit for ecosystems), Eutrophication freshwater (Eu – water, kg P equivalent), Eutrophication marine (Eu – marine, kg N equivalent), Eutrophication terrestrial (Eu – terrestrial, mole N equivalent), Human toxicity cancer – Total (HT Cancer – Total, Comparative toxic unit for humans), Human toxicity non-cancer – Total (HT no Cancer – Total, Comparative toxic unit for humans), Ionizing radiation human health (IR HH, KBecquerel U235 equivalent), Land use (LU, Point), Ozone depletion (OD, kg trichlorofluoromethane equivalent), Particulate matter (PM, disease incidences), Photochemical ozone formation human health (POF HH, kg

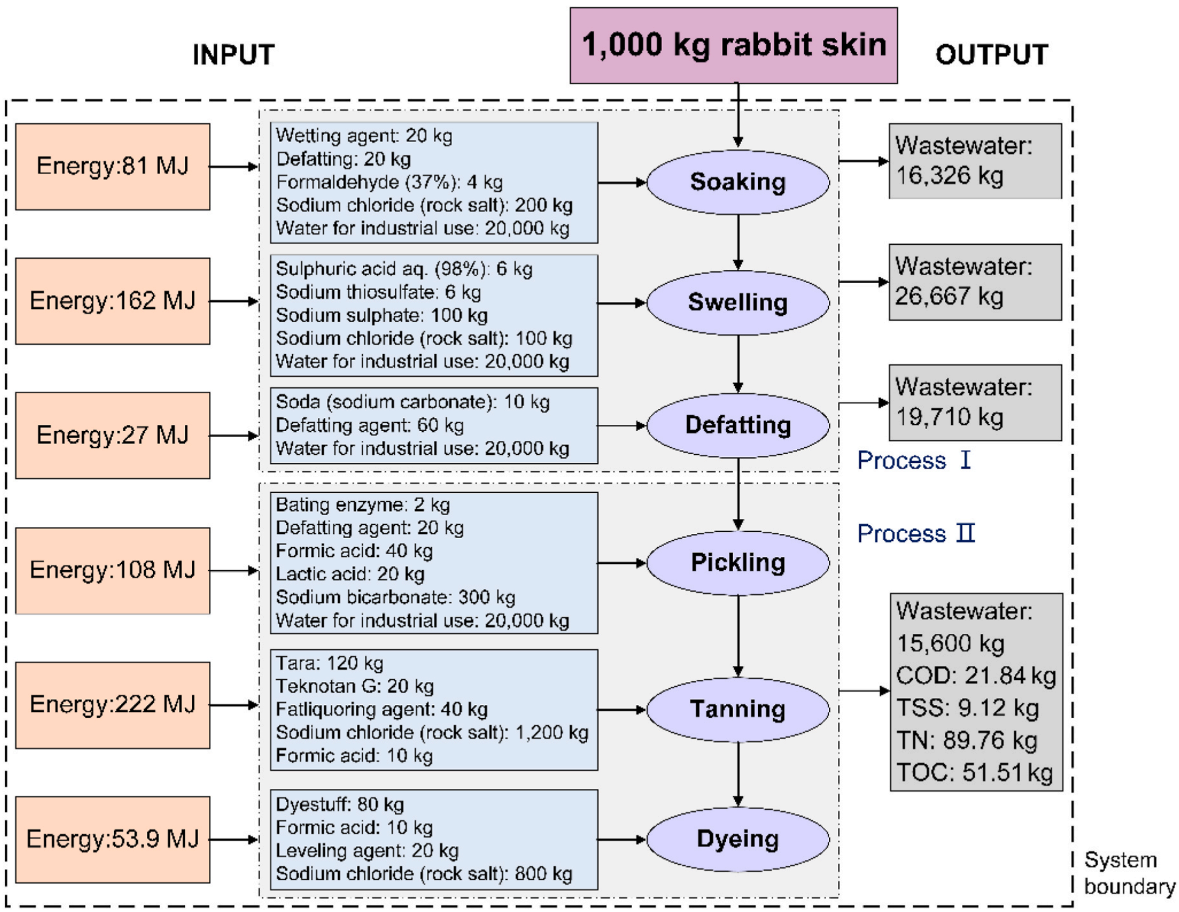

Fig. 3. Flow sheet of chemicals and energy inventory for Method III (TA-ZE) in rabbit fur leather manufacture (COD: Chemical Oxygen Demand; TSS: Total Suspended Solid; TOC: Total Organic Carbon; TN: Total Nitrogen).

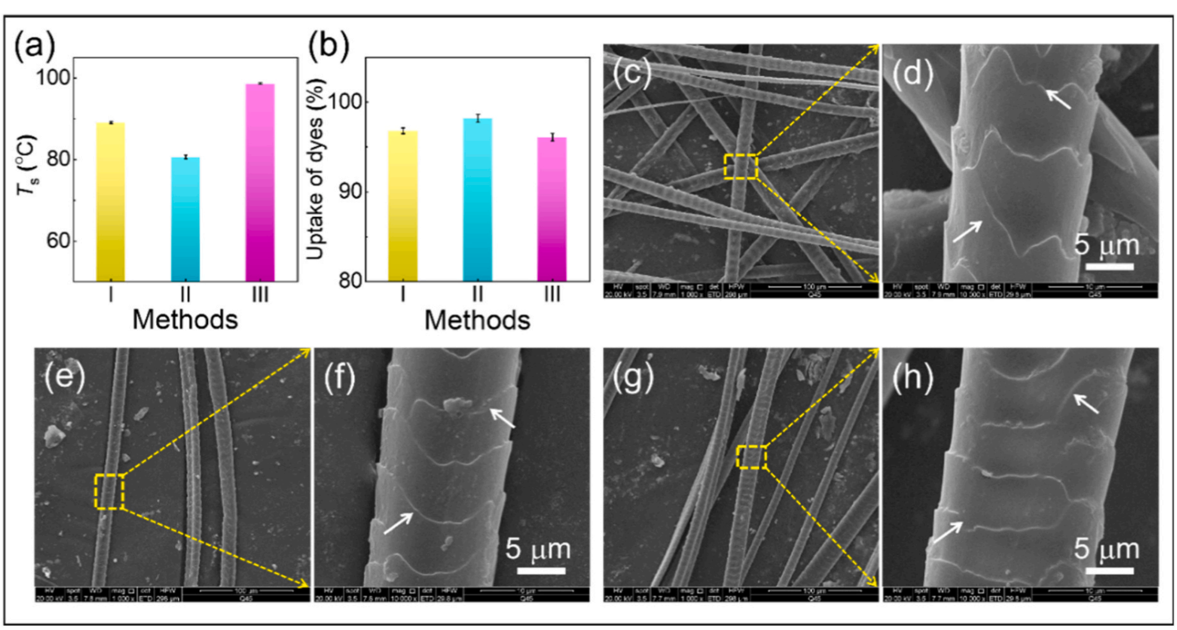

Fig. 4. (a) Shrinkage temperature (T_s) and (b) uptake of the dyestuff of rabbit fur leather manufactured by different combination tanning systems: (I) Cr–Al, (II) THPS-LA, and (III) TA-ZE, respectively. FE-SEM images and the corresponding images at a higher magnification of fleece structure of rabbit fur leather tanned by different combination tanning systems: (c, d) Cr–Al, (e, f) THPS-LA, and (f, h) TA-ZE, respectively.

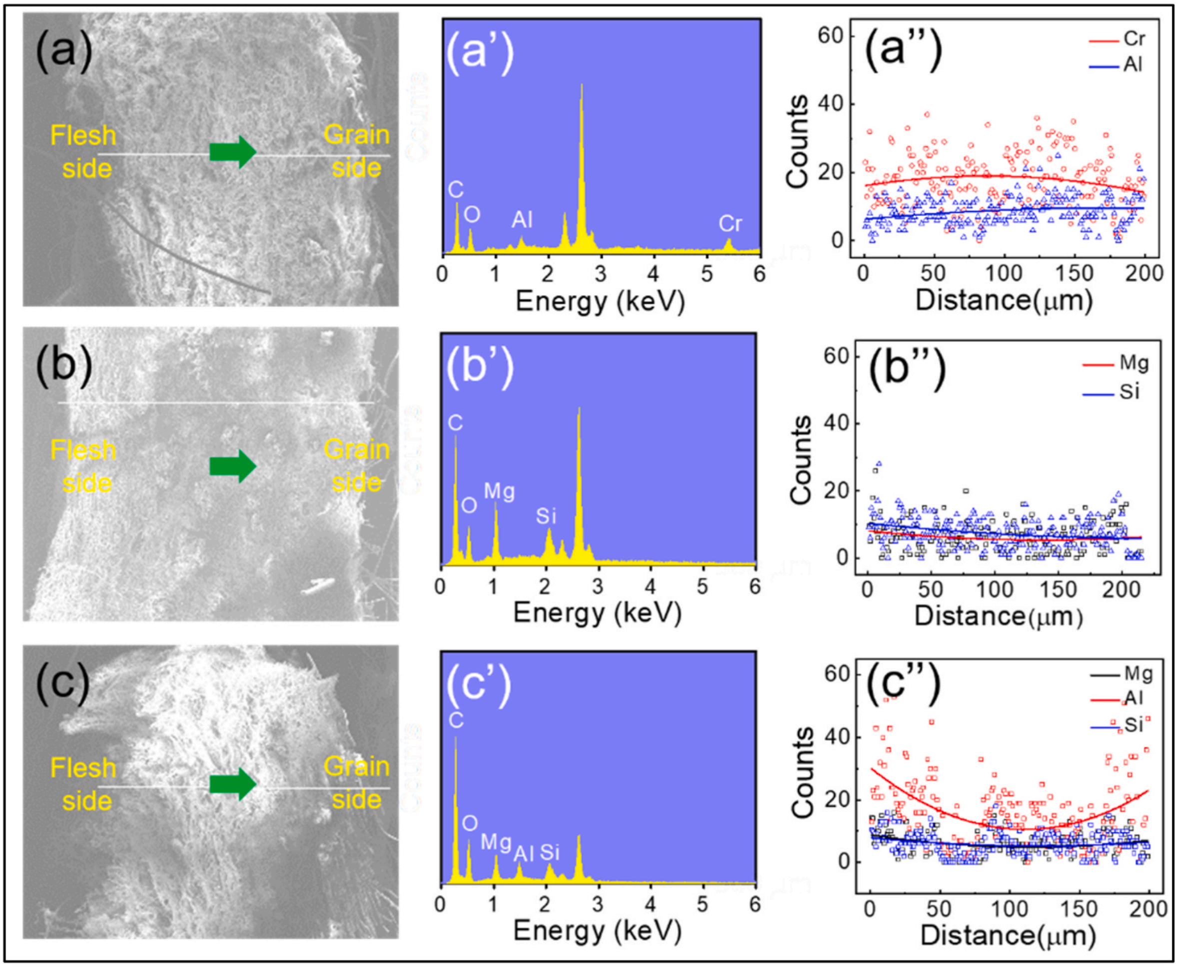

Fig. 5. SEM images, the corresponding EDX and EDS spectrum of rabbit fur leathers manufactured by different combination tanning systems: (a, a' and a'') Cr–Al, (b, b' and b'') THPS-LA, and (c, c' and c'') TA-ZE, respectively.

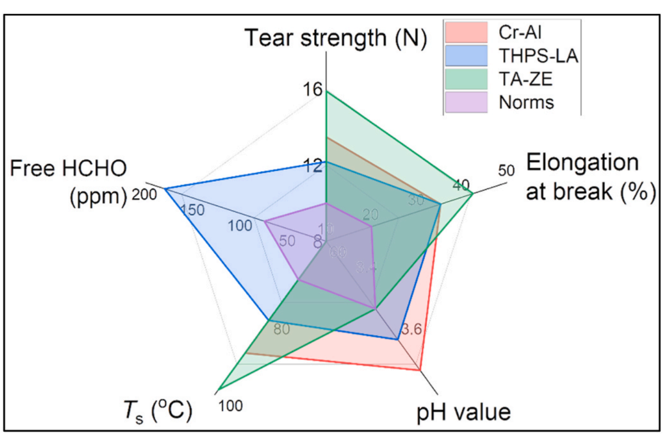

Fig. 6. Tear strength properties, pH value, shrinkage temperature, and restricted free HCHO content of rabbit fur leathers tanned by Cr–Al, THPS-LA, and TA-ZE combination tanning systems, respectively, compared to norms of current Chinese standard requirements for fur garment leather articles.

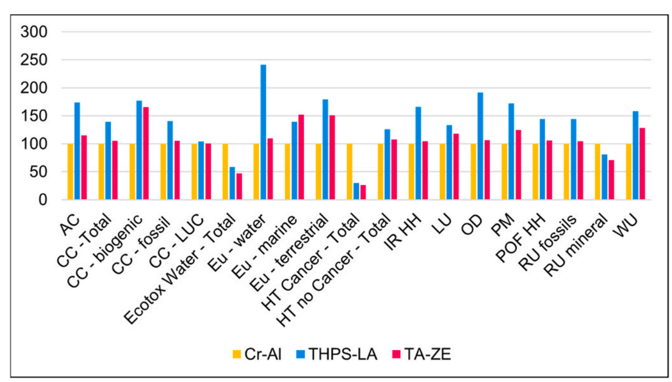

Fig. 7. Impact categories of THPS-LA and TA-ZE combination tanning systems for rabbit fur leather processing in comparison with the Cr–Al combination tanning system recommended on the method EF 3.0 (European Commission, 2023).

Non-methane volatile organic compounds equivalent), Resource use fossils (RU fossils, MJ), Resource use mineral and metals (RU mineral, kg Sb equivalent), and Water use (WU, m^3 world equivalent).

The relative impacts were calculated in comparison with conventional chromium tanning process, e.g., Method I (Cr–Al) (Fig. 7). The diagrams representing the contribution of the different steps of the process to each impact category were also shown (Figs. 8–10 for Methods I to III, respectively) for a more detailed comprehension. Finally, a discussion on the most contributing aspects (chemical substances) to each of the three methods was presented.

It should be noted that the most unsustainable method was Method II (THPS-LA), prevalent in the 16/19 impact categories, followed by the conventional Method I (Cr–Al), and finally Method III (TA-ZE). The only impact categories where Method I was worse were the HT Cancer,

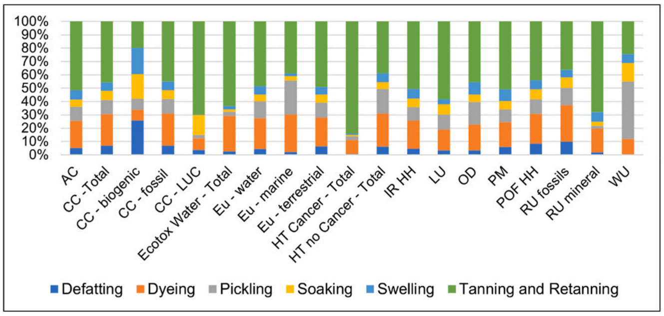

Fig. 8. Contribution of the different process steps in rabbit fur leather processing, including pre-tanning (soaking, swelling, defatting, and pickling), tanning, and post-tanning (retanning and dyeing) to the total impact of Method I (Cr–Al).

Ecotox Water, and RU minerals. These contributions of Method I (Cr–Al), mostly related to these three impact categories, were already expected due to the presence of higher amounts of metals (Cr and Al) in the recipe compared to the other two methods. In the case of Method III (TA-ZE), it was a more balanced method, as it significantly affected only the water-related impact categories (like the Eu – marine and terrestrial and Water Use impact categories) and the CC – biogenic, instead of the toxicity-related categories. Therefore, from a sustainable point of view, Method III seemed more convenient to be used for further improvements.

On the other hand, although Method II (THPS-LA) had less impact on the Ecotoxicity and Human toxicity (HT – cancer) than the conventional Method I (Cr–Al), it was less sustainable in many other impact categories. These problems, as detailed in the next section, were related to the high reactivity of organophosphate compounds (THPS), which may change many molecules in the ecosystems (Wong et al., 2019). At the same time, the phosphorous-derived compounds were strongly related to eutrophication, although sometimes they were used as pesticides, and they could also become good growing agents (phosphorous was one of the main fertilizing elements) (Lucy and Robert, 2018).

Regarding the most contributing process steps, for Method I (Cr–Al), the most significant one was the tanning-retanning step (prevalent in the 17/19 impact categories), followed by the dyeing, defatting, or pickling step (Fig. 8). In the tanning-retanning step, the most problematic substances were K_2SO_4 and NaCl followed by chromium. These substances were all salts from the mining origin, and the sustainability of mining was an issue (Worrall et al., 2009). Potassium was an important fertilizer, and its action was stronger in the impact categories above, such as the eutrophication (Naeem et al., 2014). The main problem in the dyeing step was the dyestuff, particularly hazardous for the presence of phenylenediamine derivatives (El-Ansary et al., 1983), followed by the defatting step due to the detergents and salts (Rosa et al., 2017).

As shown in Fig. 9, in the case of Method II (based on the THPS-LA combination tanning system), the most contributing one was the tanning-retanning step in the 12/19 impact categories, followed by the pickling (6/19 impact categories) and dyeing processes. Here, the tanning was less important than that in the previous Method I due to the increased contribution of the pickling recipe and its wastewater. Nevertheless, the tanning-retanning step was still the most contributing step to the majority of impact categories due to the organophosphate product (THPS). In fact, it affected all the categories related to its safety data, which was well-known in the reported literature (Moiseev and James, 2020). The second most impactful chemical was NaCl, mainly due to the high amount used. The higher contribution of pickling here compared to Method I (Cr–Al) was resulted from the use of $NaHCO_3$.

Finally, as displayed in Fig. 10 for Method III (based on the TA-ZE combination tanning system), the main impact process was surprisingly the pickling step, prevalent in the 17/19 impact categories, followed by the dyeing and tanning-retanning. In the pickling, the most problematic chemical was mainly $NaHCO_3$, used with high amounts, followed by the WWT, which used the electricity and still released some pollutants to the environment. In the production of $NaHCO_3$, although CO_2 was requested and consumed, the method was in part synthetic (Solvay production) (McKee and Kauffman, 1981), and in part from the mining (high CO_2 equivalent emission). In particular, the mining process had a high impact on the ecosystem due to the extraction and transportation (with other auxiliary steps). In the dyeing, as explained before, the dyestuff followed by formic acid were the main contributing chemicals. In the end, the tanning step contributed more to the CC – LUC impact category due to the use of Tara tannin (a tanning agent from natural sources) (Hu et al., 2023). However, the TA-ZE combination tanning system was still faced with potential challenges when implemented on a larger scale, such as the high prices and unstable supply of vegetable tannins, and the acceptance of tanneries and consumers (Xiao et al., 2023). Feasible strategies, such as incorporating the use of

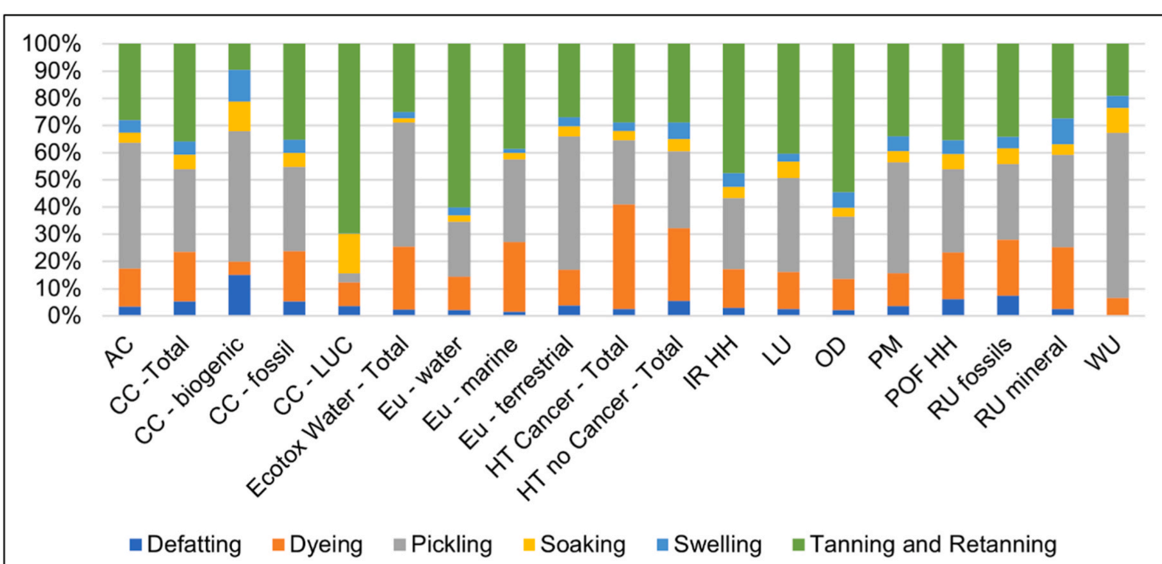

Fig. 9. Contribution of the different process steps in rabbit fur leather processing, including pre-tanning (soaking, swelling, defatting, and pickling), tanning, and post-tanning (retanning and dyeing) to the total impact of Method II (THPS-LA).

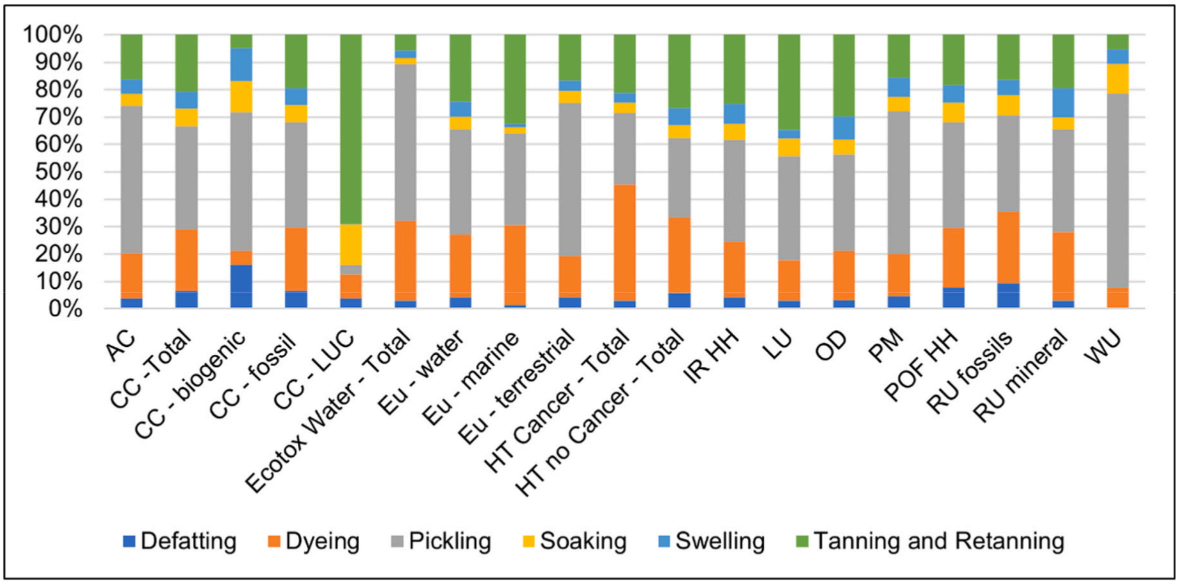

Fig. 10. Contribution of the different process steps in the rabbit fur leather processing, including pre-tanning (soaking, swelling, defatting, and pickling), tanning, and post-tanning (retanning and dyeing) to the total impact of Method III (TA-ZE).

reactive syntans to the TA or partially replacing it with other environmentally friendly tanning materials, may overcome the limitations of the combination tanning system. It was also possible to upgrade the quality and competitiveness of commercial leather products in the leather industry, and strengthen the promotion of new eco-friendly leather articles by the regulatory bodies for wide recognition from global tanneries and consumers.

Regarding the uncertainty analysis, the most significant variables corresponded to the choice of proxies representing chemical products used in the pickling (formic acid), tanning (basic chrome sulfate, THPS, or Tara), and dyeing (formic acid and dyestuff) in this study. These proxies, as said before, were modelled by using the best available data (with the best "proxy" substances available), and the data were at most five years old. The following results showed the most contributing chemicals to the environmental impact of each of the compared tanning systems:

- For Method I (Cr–Al), K_2SO_4 and NaCl were the most contributing chemicals, followed by chromium (used in the tanning-retanning, the most contributing step to this tanning system).
- For Method II (THPS-LA), THPS was the most contributing chemical (used in the tanning-retanning, also the most contributing step here).
- For Method III (TA-ZE), $NaHCO_3$ was used in high amounts during the pickling (the most contributing step to this system).

Among the above-mentioned chemicals, the only ones modelled with proxies were THPS and chromium. Hence, the higher uncertainty of the present results was due to the modeling of THPS (in Method II) and, to a less extent, chromium (in Method I). Obtaining the environmental profiles for the production of these two chemicals from representative practical production processes would improve the accuracy of the present results.

Based on the results presented above, some general ways used for eco-friendly leather manufacture could be suggested as follows:

- The use of chromium should be limited, because it is usually problematic from an environmental point of view. Natural-based tanning agents and techniques can be developed, as shown here in the TA-ZE combined tanning system;
- The use of resources should be optimized, such as water and energy, allowing the leather processing to be more competitive with other materials production and addressing the circular economy and cost reduction in the economic and social terms to grow in a sustainable way.

4. Conclusions

In this work, two nanosilicates-based chrome-free combination tanning systems were developed for eco-friendly leather manufacture. The physical performances and environmental impacts were assessed, demonstrating enhanced performances compared to the conventional tanning process. The TA-ZE combination tanning system produced the leathers with favorable properties and without limited hazardous substances, e.g., Cr(VI) and free formaldehyde, which successfully met the official standard requirements of the physical properties for fur garment leather articles. All resultant fur leathers possessed similar and integrated fleece structures. The LCA results indicated that, although the THPS-LA combination tanning system exhibited similar characteristics to the Cr–Al combination tanning system in the final rabbit fur products, higher impacts in many impact categories could be obtained. Notably, among these three tanning systems, the TA-ZE combination tanning system showed better environmental perspectives in the final fur leather products. Therefore, the TA-ZE combination tanning system showcased great promise as a suitable substitute for conventional chromium tanning systems towards eco-friendly leather manufacture. These comprehensive insights into emergent chrome-free leather processing from both technical and environmental perspectives can offer a powerful reference for manufacturing eco-friendly leather products for more sustainable practices.

CRediT authorship contribution statement

Jiabo Shi: Conceptualization, Funding acquisition. **Li Sheng:** Investigation, Writing – original draft. **Omar Salmi:** Writing – review & editing. **Maurizio Masi:** Funding acquisition. **Rita Puig:** Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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