Bio-based materials processed from protein waste for circular technologies development in the leather industry

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Introduction

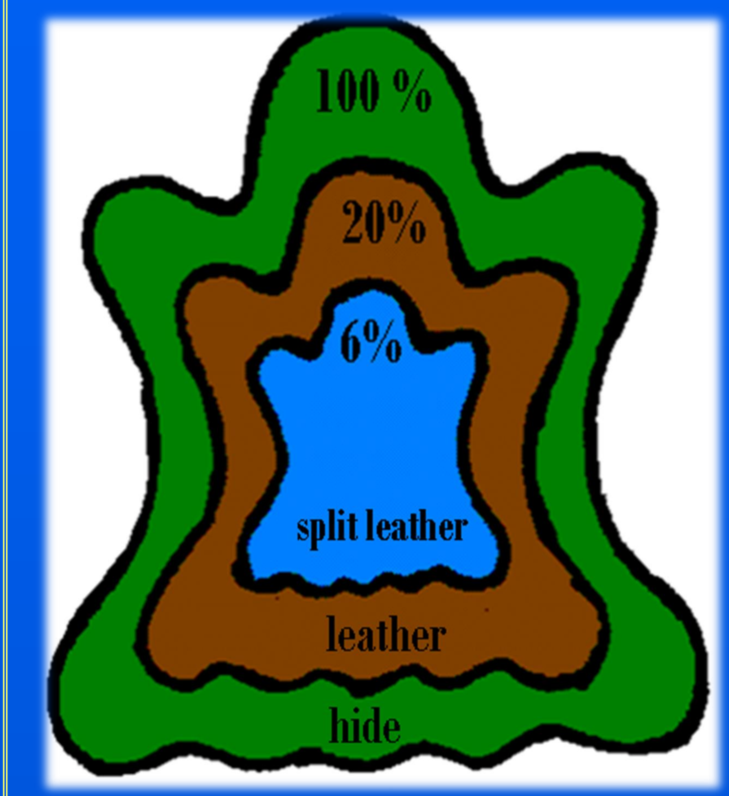

Figure 1: 26% leather and 74-80% protein hide & leather waste

The leather industry is the oldest industry that utilizes animal skin, a waste of the food industry.

Although the ecological impact of the 8 million tons of hides processed annually in the world represents a reduction of 5 million tons of greenhouse gases (equivalent to the greenhouse gases produced by 1 million cars [*www.euroleather .com*]) and the creation of products with added value, nevertheless leather processing generates important amounts of protein waste (Fig 1), which are mostly stored.

Figure 2: Circular recovery & recirculation of leather waste

Leather products are durable materials, processed with chemical containing heavy metals (CrIII), made from raw materials of petroleum origin (acrylic polymers, condensation syntans, phenol-formaldehyde resins, fatliquoring agents), or with energy-consuming chemicals (ammonium salts).

In our research, we have recovered the collagen and keratin hydrolysates of leather and hair waste from the leather industry and we prepared new deliming and retanning composites as alternatives to ammonium salts and petroleum-origin materials (Fig.2).

Results & Discussion

►Composites with tanning or filling properties were prepared by using collagen or keratin hydrolysates originated from leather processing according to the scheme from Fig.3.

►Collagen and keratin hydrolysates were additivated with organic acids and showed good ability for calcium chelating from pelts after liming process (unhairing). The scheme from Fig. 4 shows the preparation flow steps for new deliming products, alternatives to ammonium salts.

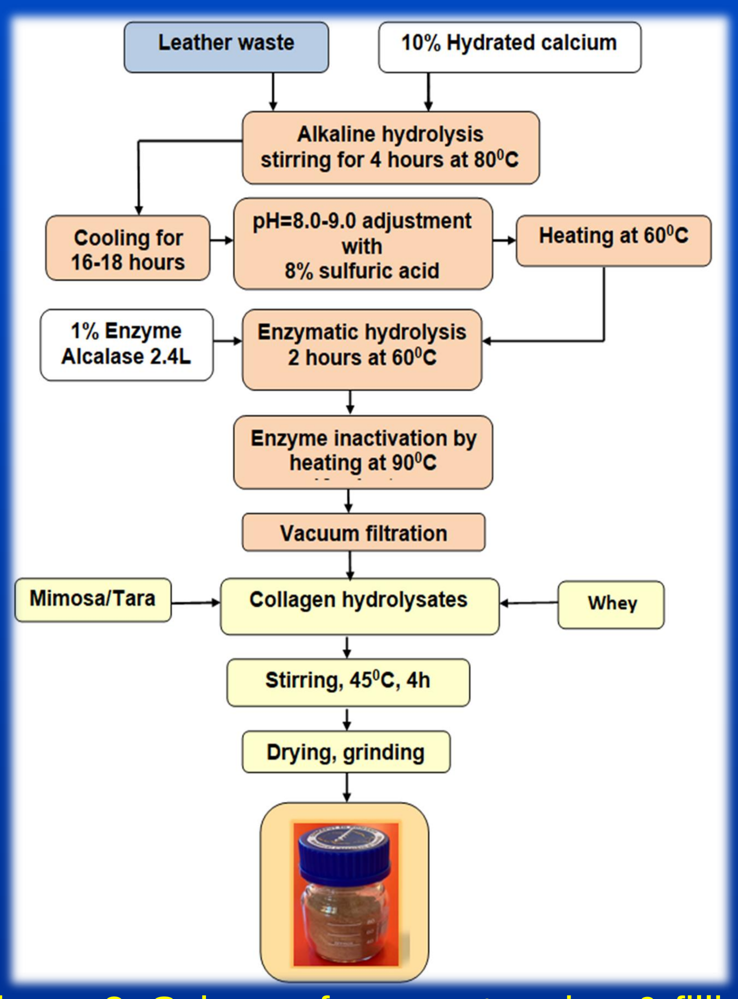

Figure 3: Scheme for new tanning & filling composite preparation

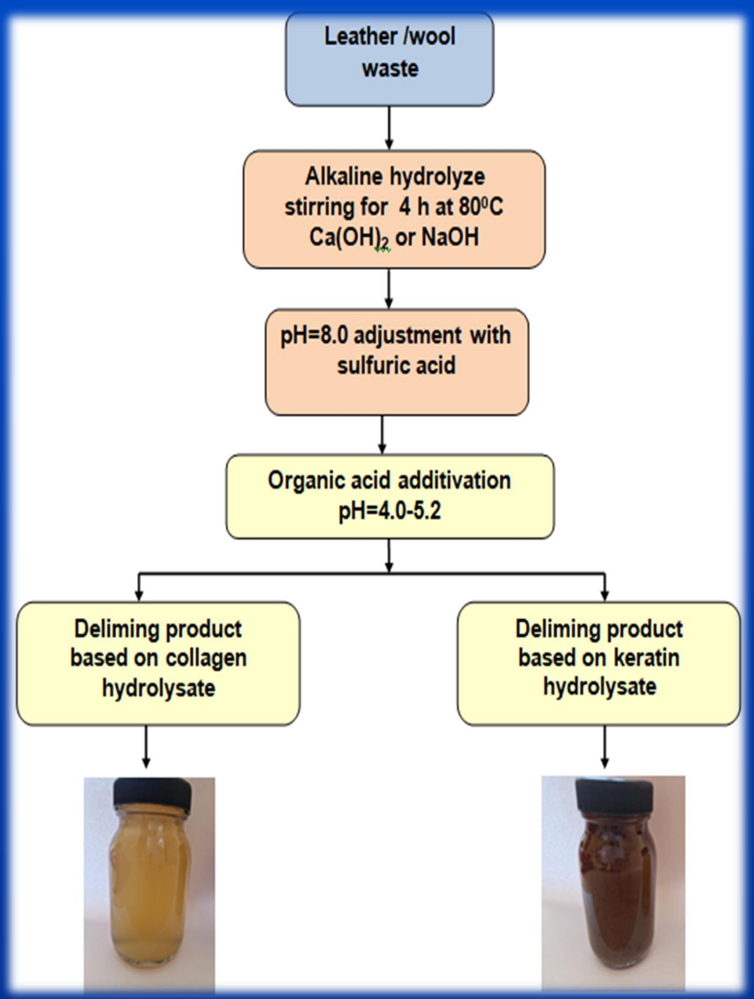

Figure 4: Scheme for new deliming products

Table 1: Physical-mechanical characterization of crust leathers delimed with new keratin-based deliming products (HK-1, HK-2), as compared to ammonium salts (Control)

Characteristics	Samples/Values			Uncertainty	Standards
	HK-1	HK-2	Control		
Thickness, mm	2.33	2.24	2.19	±0.08	SR EN ISO 2589:2016
Elongation at break, %	17.73	20.33	18.50	±1.33	SR EN ISO 3376:2020
Tensile strength at break, N/mm²	9.34	24.55	9.23	±1.33	SR EN ISO 3376:2020
Tear strength, N	102.88	99.15	104.35	±3.65	SR EN ISO 3377-1:2016
Softness, mm	5.1	4.0	4.4	±0.50	SR EN ISO 17235:2016

Table 2: Physical-mechanical characterization of crust leathers retanned with keratin-based composites (R-1, R-2) as compared to Control sample

Characteristics	Samples/Values			Uncertainty	Standards
	R-1	R-2	Control		
Thickness, mm	1.63	1.79	1.78	±0.08	SR EN ISO 2589:2016
Elongation at break, %	17.02	18.87	17.68	±1.33	SR EN ISO 3376:2020
Tensile strength at break, N/mm²	9.62	8.78	6.63	±1.33	SR EN ISO 3376:2020
Tear strength, N	25.43	26.92	24.87	±3.65	SR EN ISO 3377-1:2016
Softness, mm	4.6	4.0	4.1	±0.50	SR EN ISO 17235:2016

Ecological alternatives for sheepskin tanning and cow leather retanning were prepared and tested with prospect to replace Cr(III) salts, and petroleum-origin auxiliaries. Figures 5 a) and b) show the classical tanning with Cr(III) salts and the new tanning process with renewable composites.

The calcium chelating with the new composites can be seen in Fig.5 c) and d), before deliming (red cross section with phenolphthalein) and after deliming (colourless cross section).

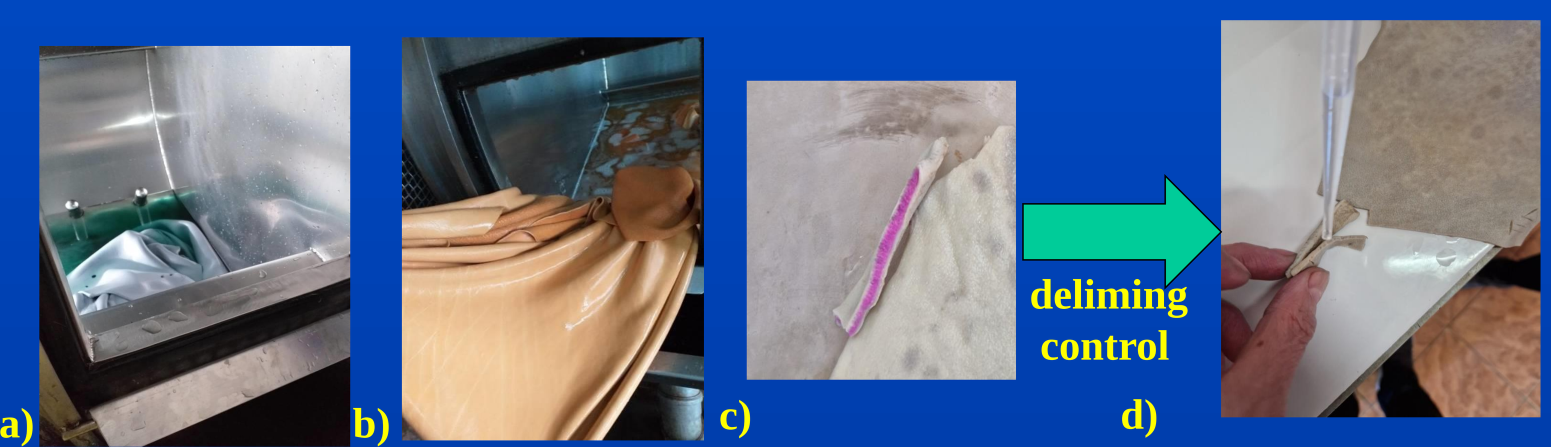

Figure 5: a) tanning with Cr(III); b)with new composite; c) pelt before deliming and d) pelt after deliming with new deliming product

►Cow leathers retanned with new composites and delimed with new deliming products showed similar properties as control leathers tanned with classical products (Table 1 and Table 2).

►Leather colour was 7.82 brighter and 7.72 yellower, which is an advantage of quality for the new leathers and composites (Fig.6).

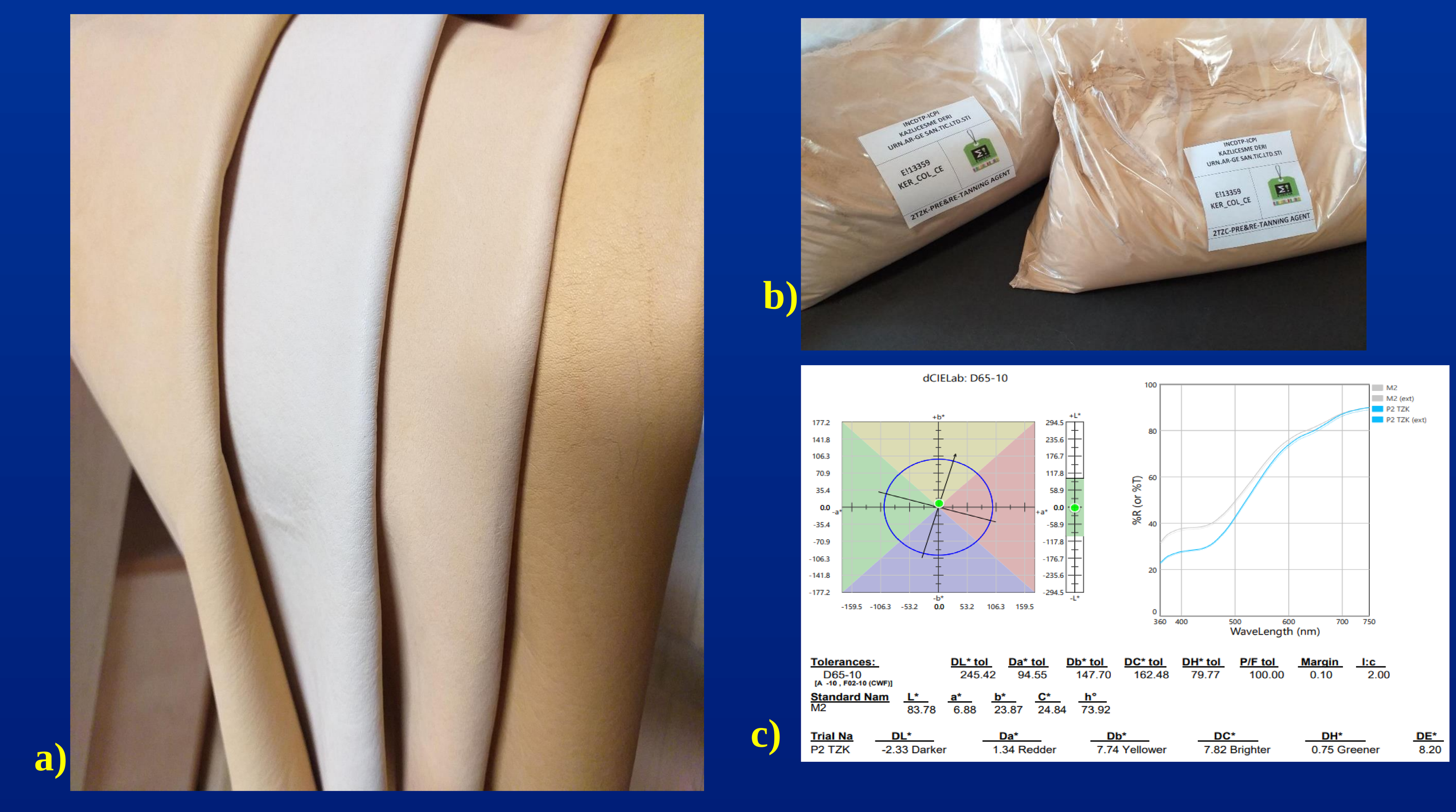

Figure 6 : a) Cow leathers retanned with the new composites (b), with more intense and brighter colour (c)

Conclusions

In conclusion, we proposed two circular technologies for leather processing by reclaiming protein waste originating from the leather industry and designing new renewable materials as alternatives to petroleum-origin materials or energy-intensive chemical reagents. The new circular technologies can add value to leather products such as lower carbon footprint and increased biodegradability.

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