Enzymes and biotechnology for cleaner leather processing

Leather processing involves three principal steps, viz. (a) purification of the multi-component skin/hide into a single protein, collagen, (b) stabilization of purified collagen matrix and (c) addition of aesthetic values for applications[1]. Leather-making is a processing industry with both socio-economic and environmental implications. Leather processing avoids environmental degradation by making use of hides collected from dead animals and as waste from the meat industry, which could have caused pollution on putrefaction. It offers socio-economic benefits through employment and from sales of leather goods. On the other hand, it has negative implications emanating from the wastes associated with industrial processing.

Conventional leather processing is associated with the discharges of significant amount of environmental contaminants. It involves about 14–15 steps comprising soaking, liming, reliming, deliming, bating, pickling, chrome tanning, basification, rechroming, basification, neutralization, washing, retanning, dyeing, fat-liquoring and fixing[2]. These steps are generally categorized into four main sets of processes: (1) pre-tanning, (2) tanning, (3) post-tanning and (4) finishing. The emission of gaseous and aqueous discharges is large. They contribute to biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), sulphides, chlorides, sulphates, chromium, lime, etc. (Figure 1)[2,3].

Conventional leather processing adopts an inefficient 'do–undo' process logic[2]. That is, at one step of leather processing, a material (chemical, etc.) is used and at the other, it is eliminated. For example[2], liming–deliming (swell–deswell), pickling–basification (acidification–basification), etc.

In the conventional method, water usage is high. It employs up to 40 l for processing 1 kg of hides[3]. About 30–40×10^{10} l of liquid effluents is produced annually with the processing of 9×10^{9} kg hides globally[3]. Thus management of effluents/pollutants and usage of a valuable resource like water in good quantity are the two main challenges faced by conventional leather processing.

In this scenario of global warming and climate change, greener technologies with zero or little wastage or pollution are always welcome.

Researchers at the Central Leather Research Institute (CLRI), Chennai have developed a novel green technology for leather processing. It uses enzymes (biocatalysts) and other integrated technological tools, and provides an alternative to the conventional 'do–undo' logic. These biotechnological methods are environment-friendly. They help in reducing COD load by 80%, TDS load by 85%, and chromium load by 80% compared to the conventional processes[2].

In the conventional method, multi-step pre-tanning and tanning processes contribute to above 90% of the total pollution[3] caused by the tanning industry. But for the same processes, the bio-mediated integrated methods (using enzymes) reduce the discharge[2] by 90%. These reductions are due to two reasons: (1) replacement of several steps through biocatalytic processes and (2) better uptake of chemicals (chromium, syntans, etc.) through product/process innovations.

Thanikaivelan *et al.*[2] have revamped the conventional processing steps resulting in what is known as 'biomediated three-step leather processing'. This biocatalytic integrated process makes it possible to avoid some steps employed in the conventional process logic. Since pH alternation is minimized in the new integrated process, the scope for formation

Flayed skin + salt – water = Cured skin
Cured skin – salt + water = Soaked skin ↑ TDS
Soaked skin + lime + Na_2S – hair = Dehaired skin ↑ BOD/COD
Dehaired skin + lime – flesh – proteoglycans = Pelt ↑ Lime sludge
Pelt + NH_4Cl – lime = Delimed pelt
Delimed pelt + NaCl + H_2SO_4 = Pickled pelt ↑ TDS
Pickled pelt + chromium + $NaHCO_3$ – Na_2SO_4 – NaCl – Cr = Cr tanned leather ↑ Cr
Cr leather + $NaHCO_3$ – Na_2SO_4 = Neutralized leather
Neutralized leather + dyes + syntans + fat liquors + HCOOH = Leather ↑ TDS/COD

Figure 1. Discharge of pollutants at various steps in conventional leather processing (Source: Thanikaivelan[1]).

Table 1. Input–output audit of chemicals and bioproducts (Source: Thanikaivelan and co-workers[1,2])

Parameter	Conventional process (kg/t of raw hides)	Three-step process (kg/t of raw hides)	Reduction (%)
Input	438	90	↓ 80
Output			
Effluent	257	33	↓ 87
Sludge	149	14	↓ 91
Leather	40	43	

Table 2. Composite liquor analysis for conventional (C) and bio-catalytic three-step (E) leather processing[a] (Source: Thanikaivelan *et al.*[2])

Type of liquor	Process	COD (ppm)	TS (ppm)	Volume of effluent (l/t of raw hides[b])	Emission load (kg/t of raw hides processed[b]) COD	TS
Composite up to chrome tanning	C	2172 ± 16	14,766 ± 32	13,305	29	196
	E	3412 ± 14	16,605 ± 38	1760	6	29
Composite up to post-tanning	C	1986 ± 16	13,868 ± 22	15,700	31	218
	E	2361 ± 18	11,478 ± 34	3796	9	44

[a]Composite liquors were collected from all the processing steps, excluding soaking. [b]Weight of hides before soaking.

Table 3. Comparison of water consumption and discharge for control (C) and bio-catalytic three-step (E) leather processing of 1 kg raw hide[a] (Source: Thanikaivelan *et al.*[2])

Unit operations	Control Input (l)	Control Output (l)	Experimental Input (l)	Experimental Output (l)
Soaking	9	8.33	9	8.33
Liming/enzyme-based dehairing	3	2.53	0.06	
Reliming/enzyme-based opening-up treatment	3	2.67	0.9	0.23
Washing	1.86	1.86	0.8	0.4
Deliming and bating	0.93	0.93		
Washing	1.86	1.86		
Pickling	0.93	0.465		
Chrome tanning	0.56	1.13	0.64	0.4
Washing	1.86	1.86	0.8	0.73
Washing	0.350	0.332	0.330	0.200
Neutralization	0.350	0.399	0.330	0.356
Washing I	0.466	0.466	0.440	0.440
Washing II	0.466	0.466	0.440	0.440
Post-tanning	0.233	0.266	0.220	0.270
Washing	0.466	0.466	0.330	0.330
Total	25.331	24.03	14.29	12.126

[a]Weight of hides before soaking.

Table 4. Cost estimates of the conventional (C) and bio-catalytic three-step tanning (E) processes (Source: Thanikaivelan *et al.*[2])

Unit operations	US$/t of raw hide Control	Experimental
Lime	24.48	
Sodium sulphide	15.92	2.65
Biodart (SPIC)		24.49
α-Amylase (SPIC)		36.73
Ammonium chloride	1.94	
Alkali bate	6.64	
Sodium chloride	3.80	
Sulphuric acid	1.37	0.30
BCS	45.55	39.18
Sodium formate	1.90	
Sodium bicarbonate	2.66	
Total	104.27	103.35

of neutral salts due to acid–base reactions is reduced. In the new method, leather-making process is reduced to a three-step operation, viz. enzymatic dehairing, fibre opening using enzymes or alkali, and pickleless chrome tanning[2,4]. This three-step process reduces the use of chemicals by 96%, TS loads by 84% and formation of dry sludge by 62%.

The new leather-processing methodology developed by the CLRI researchers is eco-friendly (see Tables 1 and 2) as it offers scope for realization of near-zero discharge objective. It also brings a significant reduction in the use and wastage of water (Table 3). This bio-catalytic integrated process is technically feasible and viable (Table 4), without compromise in the quality of processed leather.

1. Thanikaivelan, P., The Nineteenth Mid-year Meeting of the Indian Academy of Sciences, Bangalore during 4–5 July 2008.
2. Thanikaivelan, P. *et al.*, *Environ. Sci. Technol.*, 2003, **37**, 2609–2617.
3. Thanikaivelan, P. *et al.*, *Trends Biotechnol.*, 2004, **22**, 181–188.
4. Thanikaivelan, P. *et al.*, US Patent 6708531, 2004.

Abhay S. D. Rajput (*S. Ramaseshan Fellow*), H. No. 59, L. No. 1, Munshi Chak, Opp. Old Chungi, Camp Road, Talab Tillo, Jammu 180 002, India.
e-mail: abhaysdr@yahoo.co.in