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Review Article

Vegetable tanning technologies for sustainable leather production: Current advances, emerging feedstocks and future perspectives

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ABSTRACT

Traditional leather manufacturing relies heavily on chromium sulphate, which accounts for over 85% of global production because of its exceptional hydrothermal stability and economic efficiency. However, strict environmental regulations and the ecological risks associated with chromium have accelerated the transition toward chrome-free tanning systems. Vegetable tanning, which utilises plant tannins, represents an important bio-based alternative. This review examines recent advances in vegetable tanning technologies, bridging the molecular chemistry of vegetable tanning with emerging bio-based feedstocks, process intensification, and chrome-free leather production. We systematically examine the chemical classifications of hydrolysable and condensed tannins and their cross-linking mechanisms with skin collagen. It also evaluates diverse botanical matrices, moving beyond well-documented commercial extracts such as mimosa, chestnut, and quebracho to assess the potential of localised and valorised agricultural and forestry resources, including acacia varieties, *Parkia biglobosa*, *Azadirachta indica*, Tara, and regional forestry plants. Furthermore, this article addresses key limitations of conventional vegetable tanning, including prolonged processing times, low exhaustion rates, and relatively lower shrinkage temperatures (Ts), by reviewing innovative process intensification techniques such as ultrasound-assisted extraction, microwave irradiation, and combination or hybrid tanning systems. Recent studies indicate that these approaches can improve tannin extraction, penetration, exhaustion, and leather performance, with selected systems achieving Ts values approaching 90–100 °C and reductions in organic pollutant loads and unabsorbed tannin under optimised conditions. Finally, environmental performance is considered using Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and Life Cycle Assessment (LCA) indicators, highlighting both the benefits and trade-offs associated with vegetable tanning. The review provides an integrated perspective on emerging technologies and feedstocks for developing efficient and environmentally responsible chrome-free leather production.

Keywords: Sustainable leather tanning, Vegetable tannins, Emerging feedstocks, Process intensification, Chrome-free tanning, Shrinkage temperature, Leather wastewater

1. Introduction

The global leather industry faces mounting pressure to align its manufacturing workflows with the principles of green chemistry, resource efficiency, traceability, and environmental sustainability [1,2]. For over a century, chrome tanning has dominated the global market, accounting for approximately 80–85% of finished leather production. The widespread adoption of trivalent chromium (Cr(III)) salts stems from their high process efficiency, relatively low cost, and ability to produce leather with high hydrothermal stability and shrinkage temperatures (Ts) generally exceeding 100 °C [3,4]. Despite these processing advantages, conventional chrome tanning generates chromium-containing effluents and solid wastes that require appropriate treatment and management.

In particular, concerns about the potential formation of hexavalent chromium (Cr(VI)) under unfavourable environmental or processing conditions have heightened attention to chromium management and safer tanning technologies [5,6].

To mitigate these environmental liabilities, contemporary research has increasingly focused on sustainable, chrome-free tanning strategies [4,7]. Among these, vegetable tanning, one of the oldest leather preservation methods, is experiencing a technological resurgence. Vegetable tanning utilises naturally occurring, water-soluble polyphenolic compounds known as tannins to stabilise the collagen matrix of hides and skins. Depending on their botanical origin and chemical structure, tannins occur principally as hydrolysable and condensed tannins, and their molecular size and structure influence their penetration, collagen interaction, tanning efficiency, and the properties of the resulting leather [8]. Recent research has consequently moved beyond reliance on established commercial extracts towards identifying and valorising alternative plant resources, including agricultural residues, forestry by-products, and regionally available botanical materials [2,9]. Using these secondary biomass streams offers an opportunity to align vegetable tanning with circular bioeconomy strategies while reducing dependence on dedicated raw-material production.

Crucially, this industrial evolution is driven not only by environmental considerations but also by increasingly stringent regulatory and market requirements. The leather supply chain faces significant restrictions under international chemical-management frameworks, most notably the European Union's REACH regulation, which restricts certain chromium(VI) compounds in articles and leather goods [6]. Similarly, the Zero Discharge of Hazardous Chemicals (ZDHC) Manufacturing Restricted Substances List provides guidance on hazardous substances that should not be intentionally used in manufacturing processes involving leather and other materials [10]. These developments have stimulated interest in tanning systems that deliver the required leather performance while reducing dependence on chromium. Recent studies have demonstrated the feasibility of chrome-free and organic tanning approaches using vegetable tannins, including systems based on Caesalpinia spinosa and other plant-derived materials [4,7].

Despite its biodegradability and favourable renewable-resource characteristics, traditional vegetable tanning remains constrained by several technological limitations. These include prolonged processing times, relatively high water and energy requirements, slow diffusion of large polyphenolic molecules into the collagen fibre network, and incomplete exhaustion of tanning liquors, which can contribute to elevated organic loads in tannery wastewater [7,11]. Consequently, the environmental advantages of eliminating chromium do not automatically translate into a lower overall environmental burden. Vegetable tanning may generate substantial organic wastewater requiring effective treatment, while the cultivation, harvesting, transportation, and extraction of tannin-bearing biomass can also contribute to its environmental footprint [2,12]. These considerations have encouraged the development of integrated approaches that consider tannin source selection, extraction efficiency, tanning kinetics, liquor exhaustion, wastewater treatment, and resource recovery together.

Recent advances in process intensification offer promising opportunities to overcome some of these limitations. Ultrasound- and microwave-assisted extraction techniques can accelerate tannin recovery from botanical materials and improve the utilisation of underexploited plant resources [13,14]. Process intensification during tanning, including ultrasound-assisted diffusion and other mechanically or chemically assisted approaches, has also been investigated to enhance tannin penetration and reduce processing time [15]. At the same time, researchers have developed combination and hybrid tanning systems that complement the characteristics of vegetable tannins with those of other chrome-free cross-linking agents, thereby improving hydrothermal stability and mechanical performance [4,16,17]. Such developments are particularly important for extending vegetable tanning beyond traditional applications and towards modern leather products that require more consistent, higher-performance specifications.

Accordingly, the present review examines recent developments in vegetable tanning technologies for sustainable leather production, with particular emphasis on the interplay among tannin chemistry, emerging botanical feedstocks, process intensification, and chrome-free tanning systems. The review considers established commercial sources such as mimosa, chestnut, and quebracho alongside emerging and localised resources, including *Acacia species, Parkia biglobosa, Azadirachta indica, Caesalpinia spinosa* (Tara), and forestry-derived residues. It further evaluates intensified extraction and tanning approaches, including ultrasound- and microwave-assisted technologies and combination tanning systems, and assesses their effects on tannin recovery, penetration, exhaustion, shrinkage temperature, and leather performance. Finally, the review examines the environmental implications of these technologies through wastewater-quality indicators such as Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD), together with broader life-cycle considerations and opportunities for waste valorisation and resource recovery. In this context, biological and physicochemical treatment approaches for tannery effluents, including microbial remediation, phytoremediation, and chemical detoxification, provide important complementary pathways for reducing the environmental burden associated with leather manufacture [18–21]. The review therefore seeks to clarify how advances in feedstock selection and process engineering can contribute to more efficient, resource-conscious, and environmentally responsible chrome-free leather production.

2. Material and Methods

2.1 Information Retrieval and Search Strategy

A structured electronic literature search was conducted across major scientific and bibliographic databases, including Scopus, Web of Science, PubMed, ScienceDirect, and Google Scholar.

The search strategy was designed to capture both foundational studies on tannin–collagen interactions and recent advances in the engineering and application of vegetable tanning technologies. Particular emphasis was placed on literature addressing emerging botanical feedstocks, improved tannin extraction, process intensification, chrome-free and hybrid tanning systems, leather performance, and environmental sustainability.

The search terms were grouped into four principal categories:

- **Group 1 – Core tanning processes:** "vegetable tanning", "chrome-free tanning", and "organic tanning".
- **Group 2 – Botanical matrices and tannin sources:** "tannin extract", "mimosa", "acacia", "chestnut", "tara", "Parkia", "neem", "spruce bark", "quebracho", and "polyphenol".
- **Group 3 – Process intensification and performance metrics:** "ultrasound-assisted extraction", "microwave extraction", "microwave tanning", "hybrid tanning", "shrinkage temperature", and "tannin-to-non-tannin ratio".
- **Group 4 – Environmental and sustainability metrics:** "Life Cycle Assessment", "Chemical Oxygen Demand", "Biological Oxygen Demand", "tannery effluent", "waste biomass", and "resource recovery".

These terms were combined using appropriate Boolean operators and database-specific search functions. The final search logic centred on combinations of "vegetable tanning", "chrome-free", "tannin", "acacia", "vegetable extract", "waste biomass", "ultrasound", "microwave", "hybrid", "shrinkage temperature", "LCA", "effluent", and "COD". Searches were then refined to identify studies with experimentally relevant information on tannin composition, extraction conditions, tanning performance, environmental indicators, and the potential industrial application of alternative botanical resources.

Table 1. Literature-search framework used in the review

Search domain	Representative search terms	Principal information targeted
Core tanning process	Vegetable tanning; chrome-free tanning; organic tanning	Alternative tanning technologies and process principles
Botanical feedstocks	Mimosa; acacia; chestnut; Tara; Parkia; neem; spruce bark; quebracho; tannin extract	Conventional and emerging tannin sources
Process intensification	Ultrasound; ultrasound-assisted extraction; microwave extraction; microwave tanning; hybrid tanning	Extraction efficiency, diffusion, process time and tanning performance
Leather performance	Shrinkage temperature; Ts; tensile strength; grain tightness; colour; exhaustion	Hydrothermal and physical/mechanical properties
Environmental performance	COD; BOD; TDS; tannery effluent; LCA; waste biomass; resource recovery	Wastewater burden, life-cycle impacts and circularity

2.2 Inclusion and Exclusion Criteria

To conduct a focused review of the technological development and potential industrial applications of vegetable tanning, predefined screening criteria were applied.

Inclusion criteria

1. **Study design:** Peer-reviewed original research articles, short communications, and relevant technical or scientific reviews published in English-language journals were included.
2. **Technical scope:** Studies were prioritised if they provided quantitative or experimentally supported information on tannin characterisation, tannin-to-non-tannin ratios, tannin–collagen interactions, tanning performance, hydrothermal stability as expressed by shrinkage temperature (Ts), mechanical properties of the resulting leather, tanning-liquor exhaustion, or tannery wastewater characteristics.
3. **Botanical relevance:** Studies investigating established commercial tannin sources, as well as emerging, indigenous, agricultural-residue, and forestry-derived feedstocks, were considered if the material had demonstrated or reasonably evaluated relevance to leather tanning.
4. **Technological relevance:** Studies on intensified extraction or tanning processes, including ultrasound- and microwave-assisted approaches, as well as combination and hybrid tanning systems, were included if their relevance to vegetable or chrome-free leather production could be established.
5. **Temporal profile:** The primary emphasis was on literature published between 2015 and 2026 to capture recent technological developments. Earlier literature published between 1980 and 2014 was selectively retained where it provided important foundational information on tannin chemistry, botanical sources, tanning mechanisms, or established process principles.

Exclusion criteria

1. Studies that dealt exclusively with conventional chrome tanning, chromium recycling, or heavy-metal finishing, without a meaningful comparative or technological connection to vegetable, organic, or chrome-free tanning, were excluded.
2. Patents, conference abstracts, unverified industrial promotional materials, and popular-science publications lacking sufficient experimental or technical information were excluded.
3. Studies concerned solely with the medicinal or pharmaceutical extraction of plant materials were excluded if they provided no meaningful evaluation of tannin suitability for collagen interaction, leather processing, or tanning performance.
4. Studies that lacked sufficient information to link the reported tannin extraction or treatment process to

leather manufacture were not prioritised for the comparative analysis.

2.3 Data Extraction Parameters

A standardised data-extraction framework was used to organise information from the selected full-text publications. The extracted parameters were grouped into five main categories:

1. **Botanical characteristics:** plant species, botanical part used, geographical or industrial origin, and whether the material originated from a commercial plantation, agricultural residue, a forestry by-product, or another secondary biomass stream.
2. **Tannin characteristics**: tannin class (hydrolysable, condensed, or mixed), reported tannin concentration, tannin-to-non-tannin ratio, and other relevant chemical characteristics, where available.
3. **Processing conditions:** extraction method, solvent or extraction medium, temperature, extraction time, ultrasound or microwave conditions where applicable, tanning formulation, float conditions, tanning duration, and other relevant process parameters.
4. **Leather performance:** shrinkage temperature (Ts), tensile strength, grain tightness, colour characteristics, and other physical or mechanical properties reported in the individual studies.
5. **Environmental indicators:** tanning liquor exhaustion, COD, BOD, total dissolved solids (TDS), wastewater characteristics, waste generation, carbon-equivalent values, and life-cycle assessment indicators, where available.

Table 2. Principal data categories extracted from the selected literature

Data category	Parameters extracted	Purpose of comparison
Botanical source	Species, plant part, geographical/industrial origin, biomass type	Assessment of feedstock diversity and resource availability
Tannin chemistry	Tannin class, tannin content, T/N ratio	Evaluation of chemical suitability and extraction quality
Extraction/process	Extraction method, temperature, time, solvent, ultrasound/microwave conditions	Assessment of process intensification
Tanning conditions	Float conditions, tanning duration, formulation, auxiliaries	Comparison of tanning efficiency
Leather performance	Ts, tensile strength, grain tightness, colour and related properties	Assessment of product performance
Environmental performance	Exhaustion, COD, BOD, TDS, LCA indicators	Evaluation of environmental implications
Industrial relevance	Scale, process maturity, feedstock availability, commercial application	Assessment of potential scalability

2.4 Synthesis and Comparative Analysis

Following data extraction, the selected literature was synthesised using complementary qualitative and quantitative comparative approaches. The qualitative synthesis constructed comparative profiles of key vegetable-tanning resources, including established commercial materials and emerging regional or agricultural bio-wastes such as *Acacia nilotica, Parkia biglobosa, Azadirachta indica*, and spruce bark. Particular attention was given to differences in tannin chemistry, extraction behaviour, tanning performance, feedstock origin, and potential contributions to resource valorisation.

Where comparable numerical data were available, reported values were grouped by common performance indicators, including tannin content, tannin-to-non-tannin ratio, shrinkage temperature (Ts), leather mechanical properties, liquor exhaustion, and selected wastewater or life-cycle indicators. Because the studies differed in hide/skin type, extraction conditions, tanning formulations, analytical methods, and experimental scales, numerical results were compared descriptively rather than treated as directly equivalent. Reported ranges and trends were therefore interpreted in relation to their respective experimental conditions.

The synthesis also considered the technological maturity of the approaches reviewed. Laboratory-scale extraction studies were distinguished from pilot- or semi-industrial-scale investigations, where such information was available. This distinction was particularly important for assessing whether reported improvements in ultrasound-, microwave-, or hybrid-assisted systems could reasonably translate into industrial vegetable tanning.

Overall, the methodological framework linked tannin chemistry and feedstock selection to process engineering, leather performance, and environmental considerations. Following screening and selection, the review included 86 peer-reviewed articles. The resulting evidence base was then used to evaluate emerging botanical feedstocks, process-intensification strategies, chrome-free and hybrid tanning systems, and the environmental implications of modern vegetable tanning technologies.

3. Chemistry and Mechanism of Vegetable Tanning

Vegetable tannins are structurally diverse polyphenolic compounds that can be broadly classified into two major groups based on their chemical structures and susceptibility to hydrolytic cleavage: hydrolysable tannins and condensed tannins [8,11,24].

Hydrolysable Tannins: These tannins typically feature a carbohydrate-derived core, commonly glucose, with hydroxyl groups esterified to phenolic acids. Depending on the structural units present, they include gallotannins and ellagitannins. Hydrolysable tannins are relatively susceptible to hydrolysis under acidic, alkaline, or enzymatic conditions. Tara (*Caesalpinia spinosa)* and chestnut are important commercial sources of hydrolysable tannins and have been extensively investigated for leather production [4,8]. Their chemical composition and degree of esterification influence their reactivity, extractability, colour contribution, and interaction with collagen.

Condensed Tannins (Proanthocyanidins): Condensed tannins are oligomeric and polymeric flavonoid-derived compounds formed primarily from flavan-3-ol and related units. Unlike hydrolysable tannins, their interflavonoid linkages are predominantly carbon–carbon bonds, conferring greater resistance to hydrolytic cleavage. Mimosa (*Acacia mearnsii*), quebracho, and several other *Acacia* species are important sources of condensed tannins used in leather manufacture [8,11,12]. Molecular size, degree of polymerisation, hydroxylation pattern, and the proportion of non-tannin components can influence penetration into hide, binding behaviour, colour, and final leather properties [8,12]. Although condensed tannins constitute a major proportion of tannins used commercially in leather production, their relative abundance varies among botanical sources and commercial extracts; therefore, a universal percentage should not be assumed without a defined source and dataset.

The Collagen Interaction Mechanism

The tanning action of vegetable tannins arises primarily from multiple interactions between polyphenolic molecules and the collagen fibre matrix. In contrast to chrome tanning, where chromium(III) complexes substantially stabilise collagen through coordination interactions, vegetable tanning is dominated by hydrogen bonding, hydrophobic interactions, and other non-covalent associations between tannin molecules and collagen [23,24].

Hydrogen Bonding: The numerous phenolic hydroxyl (-OH) groups in vegetable tannins can interact with polar functional groups in collagen, including peptide carbonyl (C=O) and amino groups. These interactions contribute to tannin association with collagen and become particularly important when multiple binding sites are available along the protein structure [22,23].

Hydrophobic and Other Non-covalent Interactions: In addition to hydrogen bonding, aromatic regions of polyphenolic molecules can engage in hydrophobic and π-related interactions with suitable amino acid residues and non-polar regions of the collagen structure. These interactions can act cooperatively with hydrogen bonding and other intermolecular forces, thereby increasing tannin retention within the collagen matrix [22,23]. The extent and strength of these interactions depend on tannin structure, molecular size, degree of polymerisation, collagen accessibility, pH, temperature, and processing conditions.

Because the principal interactions in conventional vegetable tanning are predominantly non-covalent, effective stabilisation depends on the cumulative effect of numerous interactions distributed throughout the collagen fibre network. Tannin deposition within the interfibrillar spaces also produces a characteristic filling and masking effect that contributes to the distinctive handle, fullness, firmness, and appearance of vegetable-tanned leather. Comparative studies of vegetable- and chrome-tanned goat leathers have demonstrated differences in physical and functional properties, reflecting the distinct chemistry and fibre-fixation mechanisms of the two tanning approaches [16,17]. These differences are particularly important when selecting vegetable tanning systems for applications requiring specific combinations of firmness, flexibility, fullness, and hydrothermal stability.

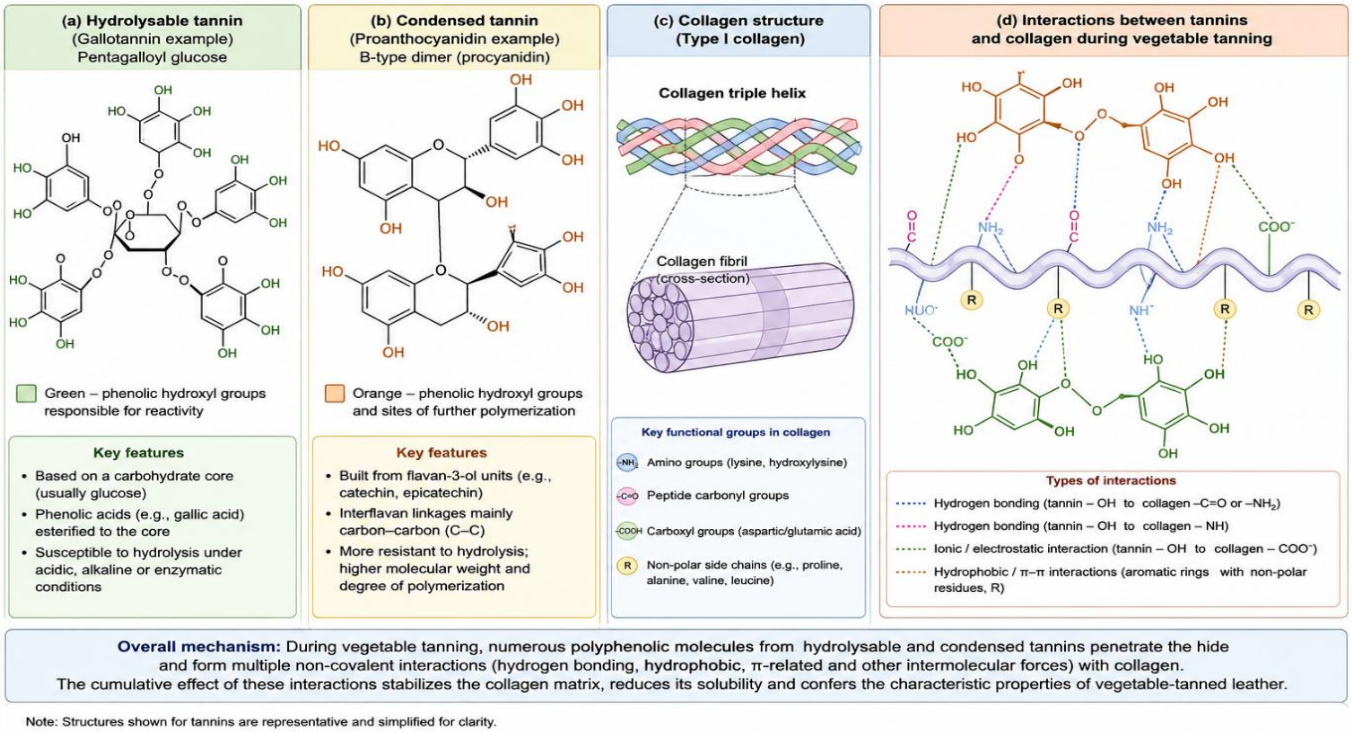


Figure 1. Schematic representation of the principal chemical classes of vegetable tannins and their interactions with collagen during vegetable tanning.

4. Evaluation of Key Botanical Matrices

Historically, the leather sector has relied on a relatively narrow range of commercial vegetable tanning extracts, particularly mimosa, quebracho, and chestnut [11,24,25]. However, growing interest in sustainable leather production has spurred the identification, characterisation, and utilisation of regional, indigenous, agricultural, and forestry-derived tannin resources [2,9]. This shift is particularly relevant to emerging feedstocks, as locally available biomass and industrial side-streams may reduce dependence on imported extracts and create opportunities for biomass valorisation. Nevertheless, the suitability of a botanical material for leather tanning must be assessed on the basis of its tannin composition, extract quality, availability, extraction requirements, interaction with collagen, and the properties of the resulting leather, rather than on botanical occurrence alone.

4.1 Mimosa (*Acacia mearnsii*) and Commercial Acacias

Mimosa extract, obtained primarily from the bark of *Acacia mearnsii* (black wattle), remains one of the most important commercial sources of condensed tannins for leather manufacture [8,11,25]. Its established industrial use is linked to favourable extract characteristics and to its ability to produce leather with useful fullness and physical properties. The chemical composition of mimosa extracts, including the distribution of tannin and non-tannin fractions, can influence tanning behaviour and final leather quality [8,25].

Because of its established commercial performance and availability, mimosa is frequently used as a reference material when evaluating alternative vegetable tanning extracts [8,11]. It therefore provides an important benchmark against which emerging botanical feedstocks can be assessed for tannin yield, chemical composition, penetration behaviour, leather performance, and potential industrial applicability. Commercial *Acacia* resources consequently remain important even as research expands towards more geographically diverse and underutilised sources of vegetable tannins.

4.2 Regional Acacias (*Acacia nilotica*, *Acacia albida* and *Acacia decurrens*)

Beyond commercial mimosa, regional *Acacia* species may be important local resources for vegetable tanning, particularly in arid and semi-arid regions where these species are already integrated into agricultural or agroforestry systems.

Acacia nilotica (Garad) has been investigated as an indigenous tanning material, with its bark and other plant parts yielding tannin-rich extracts relevant to leather processing [26]. Studies of tannin extracts from different tree species further underscore the importance of detailed chemical characterisation when assessing alternative bark resources [27]. The tanning performance of *A. nilotica* may vary with plant part, geographical origin, extraction conditions, and tannin composition; consequently, locally sourced materials should be evaluated using standardised extraction and leather-performance criteria before large-scale substitution for commercial extracts is considered.

Acacia albida (Gao) is important in agroforestry and silvopastoral systems, particularly in regions where the species is protected and managed for its broader agricultural and ecological value. Its relevance to this review lies mainly in its potential as a locally available biomass resource within regional production systems. However, agroforestry importance alone should not be taken as evidence of superior tanning performance, and further studies directly evaluating its tannin composition and leather-processing capacity remain necessary. *Acacia decurrens* (green wattle) is another tannin-bearing *Acacia* species of potential industrial interest. Wattle species have long been recognised as important sources of vegetable tanning materials, and their bark characteristics have sustained interest in their cultivation and utilisation [28]. As with other emerging *Acacia* resources, a comparative assessment against established mimosa extracts remains necessary to determine how tannin composition, extraction efficiency, penetration, fixation, and the resulting leather properties relate.

4.3 Chestnut (*Castanea sativa*)

Chestnut is an established source of hydrolysable tannins, particularly ellagitannin-rich fractions, and remains an important material in vegetable tanning [11,24]. Compared with condensed tannin extracts, chestnut-derived materials exhibit distinct chemical characteristics and tanning behaviour. Their relatively astringent nature and contribution to firmness have historically supported their use in applications requiring fuller, firmer leather [29].

Modern vegetable tanning formulations may combine extracts with different tannin chemistries to balance penetration, fixation, handle, and hydrothermal performance [11,25]. In this context, chestnut remains important not only as a conventional tanning material but also as a component of blended systems designed to optimise the properties of the final leather. Its continued industrial relevance shows that developing emerging feedstocks complements, rather than replaces, established commercial tannin resources.

4.4 *Parkia* (*Parkia biglobosa* and *Parkia roxburghii*)

The genus *Parkia* represents a potentially important emerging feedstock group, particularly in sub-Saharan Africa and parts of South Asia. *Parkia biglobosa* (African locust bean) is widely utilised for food and other purposes, generating plant materials and processing residues that may be investigated for value-added applications. In the context of sustainable leather production, the potential utilisation of tannin-containing Parkia biomass is therefore relevant to agricultural-residue valorisation and the development of regionally available tanning resources.

Parkia biglobosa and *Parkia roxburghii* have been botanically characterised in previous studies [30]. However, botanical characterisation should be distinguished from direct evidence of tanning performance. Further chemical and leather-processing investigations are required to establish tannin content, tannin composition, extract quality, collagen affinity, and the hydrothermal and mechanical properties achievable from these

materials. Accordingly, *Parkia* should presently be regarded as an emerging and promising feedstock requiring further standardised tanning evaluation, rather than as a direct equivalent to established commercial mimosa or quebracho extracts.

This distinction is important for developing sustainable local feedstocks. Agricultural biomass should ideally be evaluated using an integrated framework that accounts for its availability, competing uses, extraction requirements, tannin quality, leather performance, wastewater implications, and overall potential for industrial implementation [2,35].

4.5 Neem (*Azadirachta indica*)

Neem is widely known for its diverse bioactive constituents, but its bark and leaves have also attracted increasing attention for use in greener leather-processing systems. Recent investigations have specifically examined the tanning potential of *Azadirachta indica* and its possible utilisation as a plant-derived leather-processing material [31,32].

The available evidence suggests that neem-derived materials warrant consideration as alternative or supplementary tanning resources. However, their performance should be assessed in relation to the concentration and nature of the tannin fraction, as well as the effects of other extract constituents on collagen stabilisation and leather quality. Earlier work also demonstrated the use of *A. indica* in green hide and skin processing [33]. Collectively, these studies support continued investigation of neem as a locally available feedstock, particularly where the plant is abundant and its utilisation can be integrated with sustainable biomass-management strategies.

4.6 Tara (*Caesalpinia spinosa*)

Tara is an important commercial and semi-industrial source of hydrolysable tannins and has attracted considerable interest as a sustainable, plant-based tanning material [4,11,34]. Characterisation studies have confirmed substantial tannin content in tara powder, while tanning studies have demonstrated its relevance to innovative chrome-free leather-processing systems [34,35].

The significance of tara extends beyond its traditional use as a vegetable extract. Its use in modern chrome-free formulations shows how established plant tannins can be integrated into improved tanning technologies. Recent work using *Caesalpinia spinosa* as a principal tanning material for chromium-free goat leather further illustrates the ongoing technological relevance of tara-based systems [4]. Nevertheless, the environmental and economic advantages of tara remain dependent on feedstock sourcing, processing efficiency, transport, and the management of spent tanning liquors.

4.7 Forestry By-products: Spruce Bark (*Picea abies*) and *Eucalyptus*

Forestry and wood-processing industries generate substantial quantities of bark and other lignocellulosic side-streams, creating opportunities to recover and utilise tannin-containing materials. These resources are particularly relevant to the emerging-feedstock component of sustainable leather production because they can be obtained from existing industrial biomass streams rather than from dedicated tannin plantations [2,9].

Recent techno-economic and life-cycle assessments of tannin production from spruce bark have examined its potential for leather-industry applications [9]. This provides an important example of how alternative feedstocks should be assessed beyond tannin yield alone, considering extraction requirements, production economics, and environmental impacts.

Similarly, *Eucalyptus* bark has been investigated as a potential source of tannins [36]. More broadly, valorising plant wastes and forestry residues as tanning materials offers a pathway to align leather production with circular resource-use principles [35]. However, variability in bark composition, seasonal effects, species differences, and extraction efficiency remain important factors that require standardisation before consistent industrial utilisation can be achieved [10].

4.8 Quebracho (*Schinopsis* spp.)

Quebracho remains one of the principal commercial sources of condensed vegetable tannins and has long been used in leather manufacture [11,24]. Its tannins are generally characterised by relatively high molecular complexity and pronounced filling properties, making quebracho particularly relevant for applications requiring fuller, firmer leather.

Combination tanning studies have also investigated quebracho alongside other tanning agents [37]. These approaches demonstrate that conventional commercial extracts remain relevant to the technological development of modern vegetable tanning and may serve as components of chrome-free combination systems. Nevertheless, the processing behaviour of quebracho extracts should be carefully controlled, as the formation of poorly soluble tannin products and excessive surface deposition may adversely affect liquor handling or penetration under unsuitable processing conditions.

The evidence reviewed in this section suggests that the future of vegetable tanning will likely depend on a diversified feedstock portfolio rather than on reliance on a single botanical resource. Established extracts such as mimosa, chestnut, tara, and quebracho provide important industrial benchmarks, while regional *Acacia species, neem, Parkia*, and forestry-derived biomass offer opportunities for local resource development and circular biomass utilisation. The most suitable feedstocks will depend on the balance among tannin chemistry, extraction efficiency, feedstock availability, transport requirements, leather performance, environmental implications, and compatibility with intensified and chrome-free tanning technologies.

Table 3. Principal botanical matrices considered for vegetable tanning and their relevance to sustainable leather production

Botanical source	Principal tannin type/source characteristic	Status in leather tanning	Main relevance to the present review
Acacia mearnsii (Mimosa)	Predominantly condensed tannins	Established commercial benchmark	Reference material for comparison with alternative feedstocks
Acacia nilotica	Tannin-containing indigenous bark/plant material	Regional/emerging	Potential local alternative requiring standardised extraction and performance evaluation
Acacia albida	Regional agroforestry resource	Emerging/potential	Illustrates the potential role of locally managed biomass resources
Acacia decurrens	Tannin-bearing wattle bark	Established/regional potential	Alternative wattle resource with relevance to tannin production
Castanea sativa (Chestnut)	Hydrolysable, ellagitannin-rich fractions	Established commercial source	Important for firm leather and blended vegetable tanning systems
Parkia biglobosa	Tannin-containing biomass with potential agricultural residues	Emerging	Promising resource for regional feedstock development and biomass valorisation; requires further tanning evaluation
Parkia roxburghii	Botanically characterised tannin-containing material	Emerging	Requires direct studies of extract composition and leather-tanning performance
Azadirachta indica (Neem)	Complex plant extract containing tannin and other bioactive constituents	Emerging/locally available	Potential green leather-processing and supplementary tanning resource
Caesalpinia spinosa (Tara)	Hydrolysable tannins	Established/semi-industrial	Important chrome-free tanning material with continuing technological development
Picea abies (Spruce bark)	Forestry side-stream containing tannin fractions	Emerging industrial side-stream	Relevant to techno-economic and life-cycle assessment of tannin production
Eucalyptus bark	Tannin-containing forestry biomass	Emerging	Potential utilisation of forestry residues and alternative extraction resources
Quebracho (*Schinopsis* spp.)	Highly polymeric condensed tannins	Established commercial source	Important filling and tanning properties; useful benchmark and combination-tanning component

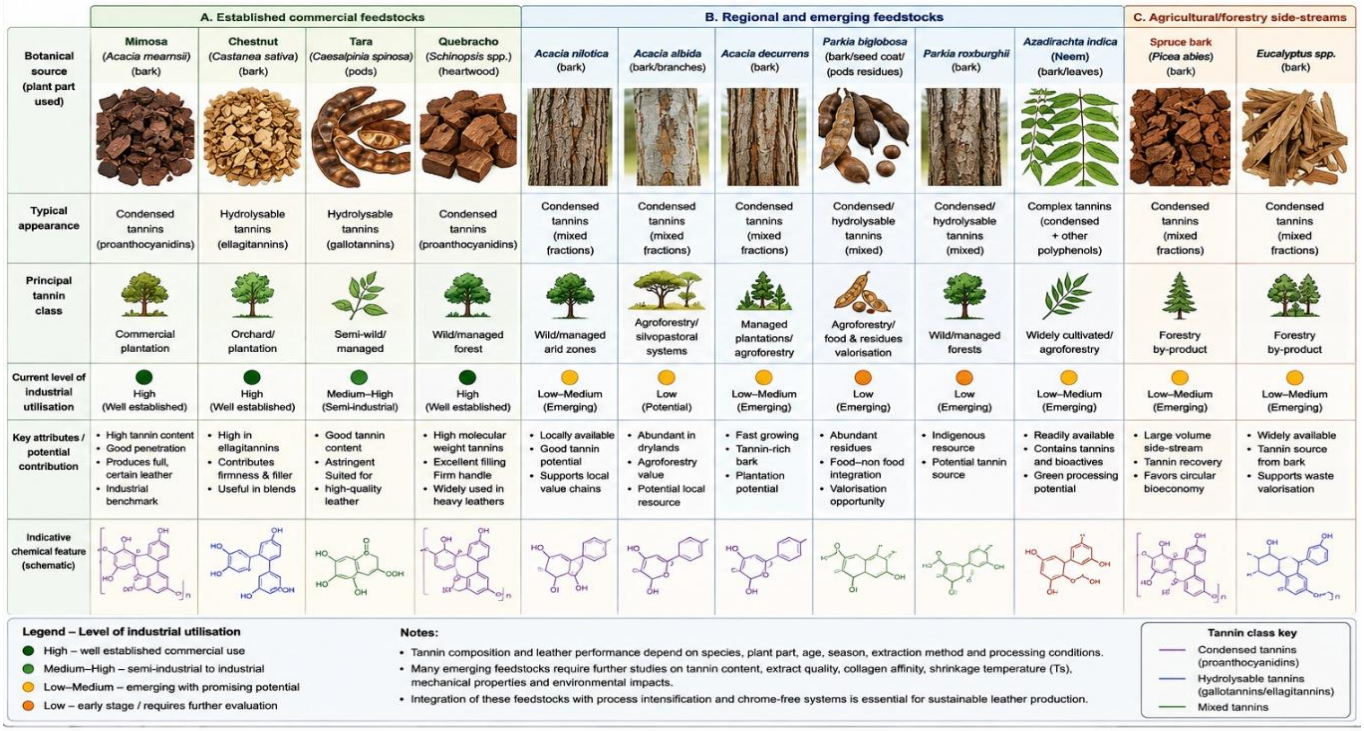


Figure 2. Summary of established and emerging botanical feedstocks for vegetable tanning, showing their principal tannin classes, biomass origin, current level of industrial utilisation, and relevance to sustainable leather production.

5. Innovative Extraction and Process Intensification Technologies

Traditional solid–liquid extraction of vegetable tannins commonly involves prolonged maceration, heating, or boiling plant materials in aqueous or aqueous-organic media. Although effective, these approaches may require substantial processing time and energy and can promote oxidation or thermal degradation of certain phenolic constituents if conditions are not adequately controlled. Recent research has therefore focused on extraction and process-intensification technologies that improve mass transfer, shorten processing time, and

enhance the recovery and utilisation of tannins while preserving their tanning functionality [38–43].

5.1 Advanced Extraction Methods

Ultrasound-Assisted Extraction (UAE)

Ultrasound-assisted extraction uses acoustic cavitation to generate localised shear forces, microstreaming, and microjet effects that can disrupt plant tissues and enhance solvent penetration. These effects facilitate the release and diffusion of soluble phenolic compounds and tannins from bark, leaves, fruits, and other botanical matrices. Studies on *Acacia mearnsii*, guava leaves, and oak bark have shown that optimised ultrasound conditions can shorten extraction times and improve recovery of tannin-rich fractions compared with conventional extraction [38–41]. However, extraction performance remains dependent on ultrasound power, treatment time, solvent composition, temperature, particle size, and botanical origin. Excessive sonication may also promote oxidation or structural modification of sensitive phenolic constituents; consequently, process optimisation is required rather than assuming that higher acoustic intensity necessarily produces better tannin quality.

Microwave-Assisted Extraction (MAE)

Microwave-assisted extraction provides rapid volumetric heating of polar solvents and plant matrices. This heating can increase internal pressure within plant tissues, facilitating cell disruption and the diffusion of intracellular tannins into the extraction medium. Response-surface optimisation studies have demonstrated MAE's potential for recovering condensed tannins and other phenolic compounds from various biomass resources, including *Prunus spinosa* branches and pequi (*Caryocar brasiliense*) [42,43]. Microwave-assisted extraction has also been investigated for tannin-rich plant materials intended for leather-related applications [44]. Its principal advantages include rapid heating and reduced extraction time; nevertheless, temperature control remains important, as excessive thermal exposure may alter the chemical composition of extracted polyphenols. Table 4 summarises the principal characteristics of the two approaches.

Table 4. Comparison of conventional and intensified approaches for extraction of vegetable tannins

Extraction approach	Principal intensification mechanism	Potential advantages	Important limitations
Conventional maceration/heating	Diffusion and thermal mass transfer	Simple equipment; readily scalable	Longer extraction time; higher energy demand
Ultrasound-assisted extraction	Acoustic cavitation, microstreaming and tissue disruption	Faster extraction; improved mass transfer; potentially higher tannin recovery	Requires optimisation of power, time and temperature
Microwave-assisted extraction	Rapid volumetric heating and pressure-assisted tissue disruption	Very short extraction times; efficient heating; good extraction yields under optimised conditions	Risk of overheating and phenolic degradation; equipment and scale-up considerations

5.2 Process Intensification During Tanning

A major technological limitation of conventional vegetable tanning is the relatively slow diffusion and fixation of tannin molecules within the dense, three-dimensional collagen fibre network. Tannin molecular size, degree of polymerisation, charge characteristics, and concentration, together with hide structure and processing conditions, influence penetration and fixation [24,48]. Process intensification therefore aims to improve mass transfer and chemical utilisation without compromising collagen integrity.

Microwave-Assisted Tanning

Microwave irradiation has been investigated to accelerate tanning-related mass transfer by rapidly heating water and other polar components within the treatment system. In principle, controlled volumetric heating can shorten the time required to achieve the desired thermal and diffusion conditions. Microwave-assisted processing has demonstrated accelerated tanning behaviour in leather-processing systems, although the available evidence is not yet sufficient to regard microwave treatment as a universally established replacement for conventional vegetable tanning [45]. Studies on microwave-assisted aluminium tanning also demonstrate the potential of microwave irradiation to intensify tanning kinetics, although such systems should be distinguished from purely vegetable or metal-free tanning [45].

For vegetable tanning, ultrasound-assisted diffusion offers more direct evidence of process intensification. Ultrasound can enhance liquor movement and promote the penetration of tannin molecules into the hide structure, thereby reducing diffusion limitations during tanning [46]. The effectiveness of such systems depends on acoustic intensity, treatment duration, liquor composition, mechanical action, hide thickness, and tannin characteristics.

High-Exhaustion Tanning Systems

Improving tannin exhaustion is another important route to process intensification, as incomplete uptake leaves substantial quantities of soluble organic compounds in spent tanning liquors. High-exhaustion strategies combine improved liquor management, mechanical agitation, controlled float conditions, and appropriate auxiliaries to enhance the transfer and fixation of tanning materials within the hide. Earlier work on asymmetric tanning and related low-discharge approaches demonstrated the importance of process design in reducing the release of unused tanning chemicals [47]. More recent cleaner-production

approaches further emphasise integrating process optimisation with wastewater management, rather than treating effluent control as a separate downstream operation [18,46].

Float Optimisation and Mechanical Action

Reducing the water-to-hide ratio can increase the concentration gradient between the tanning liquor and the collagen matrix, thereby improving mass transfer. Controlled mechanical drumming also promotes liquor circulation and hide flexing, which can facilitate more uniform penetration. However, low-float processing must be balanced with adequate liquor movement and hide-handling requirements to prevent uneven tannin distribution.

Polymeric and Other Auxiliaries

Selected polymeric auxiliaries and syntans may be incorporated into vegetable tanning formulations to modify tannin–collagen interactions, enhance penetration, and reduce premature surface fixation. Their effectiveness depends strongly on polymer chemistry, charge characteristics, dosage, and compatibility with the tannin system. Such auxiliaries should therefore be evaluated not only for tanning performance but also for their contribution to wastewater organic loading and overall environmental impact.

Process intensification offers several complementary routes to improve the efficiency of vegetable tanning. Rather than relying on a single technology, the most promising strategy is to integrate intensified extraction, controlled liquor conditions, mechanical action, and high-exhaustion formulations. Importantly, reported improvements in extraction yield, tanning time, exhaustion, or leather properties should be interpreted as system-specific outcomes, given the substantial variation in experimental conditions across studies.

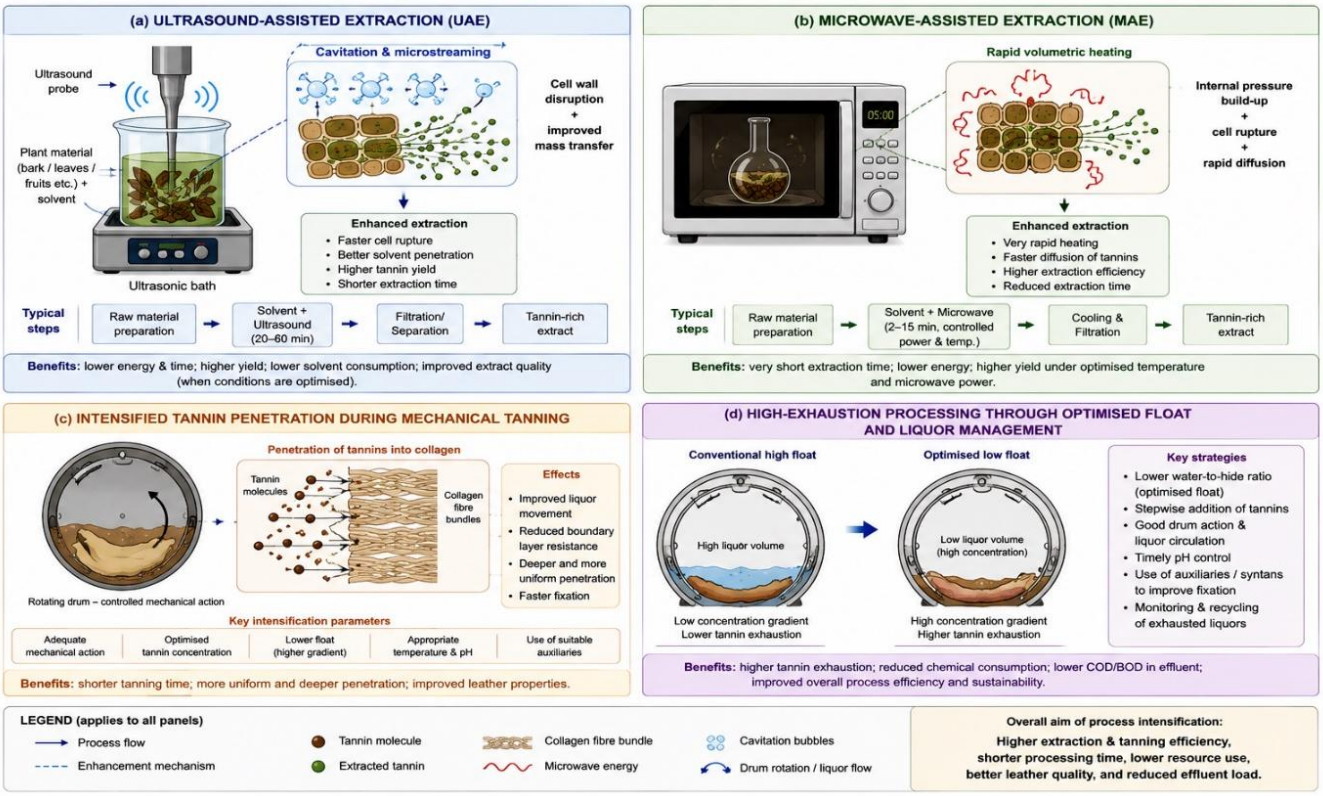


Figure 3. Schematic representation of process intensification in vegetable tanning, showing (a) ultrasound-assisted extraction, (b) microwave-assisted extraction, (c) intensified tannin penetration during mechanical tanning, and (d) high-exhaustion processing through optimised float and liquor management.

6. Hybrid and Combination Tanning Systems

While pure vegetable tanning yields leather valued for its firmness, hand feel, fullness, and natural aesthetics, its hydrothermal and processing characteristics can limit its suitability for applications requiring higher shrinkage temperatures (Ts) and shorter production cycles. Consequently, attention has increasingly focused on hybrid and combination tanning systems that integrate vegetable tannins with complementary tanning agents or functional auxiliaries [11,43]. These approaches aim to retain the desirable characteristics of vegetable tanning while improving collagen stabilisation, hydrothermal resistance, mechanical performance, tanning uniformity, and chemical exhaustion.

A key distinction is needed when discussing these systems. Chrome-free does not necessarily mean metal-free. Systems based on aluminium, zirconium, titanium, or other mineral tanning agents can eliminate chromium from the tanning process while still introducing inorganic metal species. In

contrast, genuinely metal-free systems rely on organic, polymeric, carbohydrate-derived, or other non-metallic tanning chemistries. This distinction is particularly important when evaluating environmental performance and claims about metal-free leather production.

6.1 Metal–Vegetable Combination Tanning

One established strategy combines vegetable tannins with alternative mineral tanning agents. Early pilot-scale work demonstrated that combining Tara tannins with aluminium tanning chemistry could produce high-quality bovine upper leather as an alternative to conventional chrome tanning [43]. More recent approaches have extended this concept to other mineral–organic combinations, including plant tannins with silicic-acid-based systems and aluminium-containing organic networks [44,45].

The underlying principle is the complementary stabilisation of the collagen matrix. Vegetable tannins provide multiple phenolic groups capable of hydrogen bonding and other non-covalent interactions with collagen, whereas mineral tanning species can provide additional coordination or ionic interactions with functional groups within the collagen structure. In a chrome-free combination system based on silicic acid and plant tannin, the inorganic component and plant polyphenols therefore contribute through different but complementary stabilisation mechanisms [44].

Aluminium–organic systems provide another example of this approach. Aluminium-containing oligosaccharides or related metal–organic structures have been investigated as multifunctional cross-linking systems, in which metal centres interact with collagen functional groups while the organic components provide additional interactions with the protein matrix [45]. Such approaches are promising because they may improve hydrothermal stability and mechanical performance without introducing chromium. However, the environmental profile of a chrome-free mineral system should not automatically be assumed to be superior to that of every vegetable- or metal-free system.

Recent combination-tanning studies further demonstrate the applicability of this strategy to practical leather production. Combination tanning has been evaluated as a potential alternative to conventional chrome tanning for shoe-upper leather, with attention to the resulting physical and mechanical performance [46]. These studies support the concept that combination systems can be tailored to the performance requirements of a particular leather application rather than relying on a single tanning chemistry.

Table 5. Comparison of major hybrid and combination tanning approaches

Tanning approach	Principal components	Main stabilisation mechanism	Potential advantages	Principal limitations
Vegetable tanning	Plant tannins	Hydrogen bonding and multiple non-covalent interactions	Renewable feedstocks; characteristic handle and appearance	Longer processing; potentially high organic loading
Metal–vegetable combination	Plant tannin + mineral tanning agent	Polyphenol–collagen interactions combined with mineral coordination/ionic interactions	Improved hydrothermal stability and mechanical performance	Still introduces mineral residues; not metal-free
Silicic-acid–plant tannin system	Silicic acid + plant tannin	Complementary inorganic and polyphenolic interactions	Chrome-free processing and additional collagen stabilisation	Formulation-specific performance and environmental considerations
Polymeric/organic auxiliary-assisted system	Vegetable tannin + functional polymer/auxiliary	Charge modification, bridging and additional organic interactions	Potentially improved penetration, exhaustion and post-tanning performance	Auxiliary synthesis and environmental profile require assessment
Metal-free hybrid system	Plant polyphenols + carbohydrate/organic auxiliaries	Multiple organic and non-covalent interactions	Avoids chromium and intentionally added metal tanning agents	Performance must be demonstrated for the intended application
Phosphonium–vegetable combination	Vegetable tannin + phosphonium chemistry	Complementary organic stabilisation	Chrome-free/low-chrome alternative	Chemical safety, persistence and environmental profile require assessment

6.2 Bio-Based and Polymeric Tanning Auxiliaries

A second research direction involves the use of bio-derived organic components and functional polymers as complementary tanning auxiliaries. These materials can be introduced to modify collagen–tannin interactions, improve tannin penetration, increase exhaustion, or enhance the physical properties of the resulting leather. However, their role should be distinguished from that of a primary tanning agent, as some polymeric materials reported in the literature function primarily as auxiliaries or fatliquors rather than as direct collagen cross-linkers.

Combination systems based on organic components can also help reduce dependence on chromium. For example, chestnut tannin combined with tetrakis(hydroxymethyl)phosphonium sulfate (THPS) has been investigated as a chrome-free combination tanning system [48]. Such systems should be described specifically as chrome-free combination tanning, rather than automatically as bio-based or metal-free, because their environmental classification depends on the chemical nature and life-cycle impacts of all components used.

Earlier phosphonium-based studies likewise demonstrated the potential of combining vegetable tannins with phosphonium chemistry to reduce reliance on chromium [50,51]. These studies are relevant to the development of organic combination tanning and provide an important link between conventional vegetable tanning and more recent metal-free approaches.

Polymeric auxiliaries represent another complementary strategy. Amphoteric copolymers have been investigated for sustainable fatliquoring of both chrome and chrome-free leathers, with reported improvements in uptake and selected leather properties [52]. Their role is therefore best understood as enhancing process and performance, rather than necessarily as a replacement for the primary tanning mechanism.

6.3 Genuinely Metal-Free Hybrid Tanning Systems

A distinct category comprises tanning systems in which no metal tanning salt is intentionally used as the principal tanning or cross-linking agent. This distinction is important because aluminium-, titanium-, and zirconium-containing systems are chrome-free but remain mineral-containing tanning processes. Recent research has investigated metal-free hybrid systems that combine plant polyphenols with carbohydrate-derived auxiliaries [47]. The aim is to create an effective network of organic interactions that stabilises collagen while avoiding chromium and other metal tanning agents. Such systems are particularly relevant to developing tanning processes that integrate renewable organic resources and reduce dependence on inorganic tanning chemistry.

Another emerging example is poly(carbamoyl sulfonate)-based metal-free tanning, which has been investigated as an alternative tanning chemistry for producing leather without intentionally added metal tanning agents [49]. These systems are particularly relevant to the concept of genuinely metal-free leather, although the absence of metals alone does not establish overall environmental superiority. Chemical synthesis requirements, auxiliary consumption, wastewater characteristics, biodegradability, leather performance, and end-of-life behaviour must also be considered. The distinction among chrome-free, metal-free, and bio-based systems can therefore be summarised as follows:

- **Chrome-free systems:** no chromium-based tanning agent is intentionally used, although other metals may be present.
- **Metal-free systems:** no metal-based tanning agent is intentionally used as the primary tanning chemistry.
- **Bio-based systems:** the tanning agent, or a substantial proportion of the formulation, is derived from renewable biological resources; this does not necessarily mean the system is metal-free.
- **Bio-based metal-free systems:** combine renewable organic components with the deliberate avoidance of metal tanning agents, and therefore represent the most stringent combination of the two concepts.

This terminology matters when interpreting environmental claims because removing chromium addresses one environmental concern but does not, on its own, establish overall sustainability.

6.4 Performance and Industrial Considerations

The principal attraction of hybrid tanning is the potential to balance the characteristic properties of vegetable-tanned leather with improved hydrothermal and mechanical performance. Comparative evidence indicates that vegetable-tanned leather can exhibit satisfactory tensile and physical properties, although performance varies substantially with botanical source, tannin composition, tanning conditions, and leather application [53]. Combination systems may therefore offer a means of tailoring performance for applications such as shoe uppers, upholstery, and other technically demanding leather products.

However, reported improvements in Ts, tensile strength, exhaustion, or softness should be interpreted on a system-specific basis. Differences in hide or skin origin, tannin concentration, tanning time, pH, float, auxiliary dosage, mechanical action, and analytical methods make direct numerical comparisons between studies difficult. A high Ts obtained in one laboratory formulation should therefore not be presented as a universal characteristic of a particular tanning technology.

The most promising direction is therefore not the replacement of one tanning chemistry with another in isolation, but the rational combination of complementary mechanisms. Vegetable polyphenols can provide renewable organic interactions with collagen; mineral components can provide additional coordination where acceptable; and polymeric or carbohydrate-derived auxiliaries can modify mass transfer, charge interactions, and exhaustion. Metal-free systems extend this strategy further by attempting to reproduce the stabilising effects of combination tanning using exclusively organic or bio-derived chemistries [47,49,52].

From an industrial perspective, selection among these approaches should ultimately be based on a combination of leather performance, processing time, chemical consumption, exhaustion, wastewater characteristics, material availability, cost, and life-cycle impacts. This broader assessment is particularly important for distinguishing a technically successful chrome-free process from a genuinely more sustainable one.

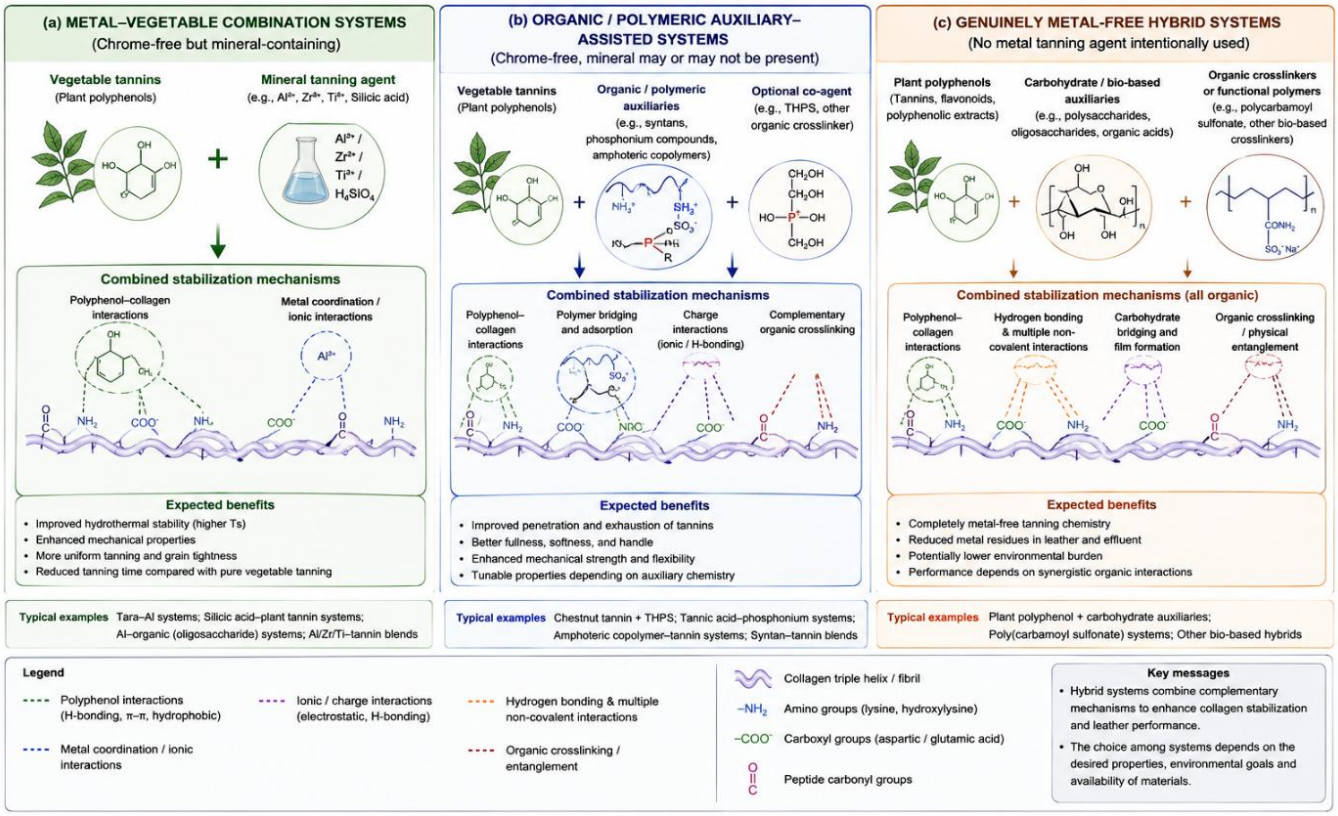


Figure 4. Schematic representation of hybrid and combination tanning pathways, distinguishing (a) metal–vegetable systems, (b) organic/polymeric auxiliary-assisted systems, and (c) genuinely metal-free hybrid systems.

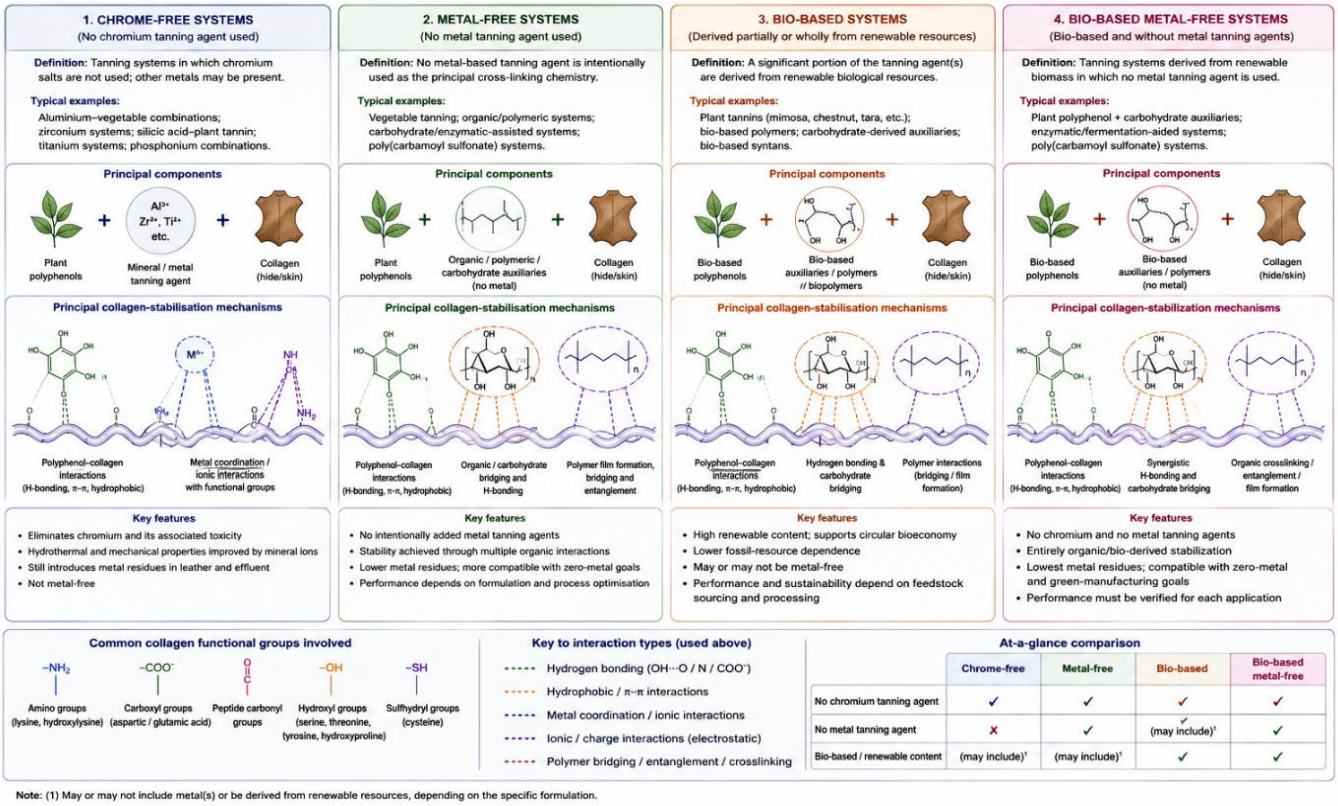


Figure 5. Conceptual classification of chrome-free, metal-free, bio-based, and bio-based metal-free tanning systems and their principal collagen-stabilisation mechanisms.

Hybrid and combination tanning systems serve as an important technological bridge between conventional vegetable tanning and high-performance chrome-free leather production. Future development should focus on simultaneously optimising collagen stabilisation, Ts, mechanical performance, tannin exhaustion, chemical safety, renewable feedstock content, wastewater quality, and life-cycle impacts, rather than merely the absence of chromium.

7. Environmental Footprint and Techno-Economic Considerations

Transitioning from conventional chromium processing to vegetable and other chrome-free tanning systems alters the environmental profile of leather manufacture rather than eliminating environmental burdens altogether. The principal benefits include reduced dependence on chromium-containing tanning agents, while important challenges remain regarding organic loading in wastewater, extraction of vegetable tannins, energy consumption, biomass sourcing, and solid-waste management. Consequently, environmental performance should be evaluated across the entire process chain using wastewater indicators, resource-use metrics, and life-cycle assessment (LCA), rather than by considering the tanning agent alone [5, 6, 12, 54].

7.1 Wastewater Dynamics

Vegetable tanning liquors avoid the direct introduction of chromium salts into the tanning stage, thereby reducing chromium-associated contamination in spent liquors and sludge. However, vegetable tannins are complex polyphenolic organic materials, and incomplete exhaustion can result in substantial organic loading of the wastewater. The environmental advantage of chrome-free tanning therefore depends strongly on tannin exhaustion, liquor management, water use, and the effectiveness of downstream treatment [18, 55, 56].

Biological and physicochemical treatment technologies provide complementary approaches to managing tannery wastewater. Okoduwa et al. [18] demonstrated the potential of yeast isolates to treat tannery effluent, while Yahaya et al. [19] reported the chromate-reduction capability of *Aspergillus flavus*. Chemical approaches can also contribute to removing or detoxifying residual metals, as demonstrated by Habila et al. [20] for Cr(III)- and Fe(III)-contaminated tannery wastewater. In addition, phytoremediation and biomass recovery approaches, such as using *Chlorella sorokiniana*, offer opportunities to combine effluent treatment with resource recovery [21]. These studies show that wastewater management should be an integral component of sustainable tanning rather than a separate end-of-pipe operation.

The organic nature of vegetable-tanning effluents also poses treatment challenges. Advanced oxidation and biological treatment have been investigated to degrade polyphenolic compounds and reduce COD in vegetable-tanning wastewater [55]. High-strength organic effluents from combination tanning may similarly require integrated treatment strategies [56]. Accordingly, claims of lower environmental impact should not be based solely on the absence of chromium; they should also account for COD, BOD, suspended solids, total dissolved solids, tannin residues, and treatment energy requirements.

7.2 Environmental Trade-offs and Life-Cycle Limitations

The environmental performance of vegetable and chrome-free tanning is highly system-dependent. Although eliminating or substantially reducing chromium can yield significant benefits, cultivating or harvesting tannin-containing biomass, extracting and concentrating tannins, transportation, process duration, water demand, and wastewater treatment can introduce additional environmental burdens [12, 54, 57].

Comparative LCAs have shown that the environmental ranking of tanning technologies varies by impact category and system boundary. Yue et al. [58] compared chrome tanning, chrome-free metal tanning, and metal-free tanning systems, demonstrating the importance of evaluating alternative tanning routes across multiple environmental indicators rather than assuming a single technology is universally superior. Similarly, reviews of green-chemistry approaches to leather tanning emphasise the need to consider chemical consumption, energy use, waste generation, and process efficiency together [59].

The source of the tannin is particularly important. Tannin feedstocks from dedicated plantations may entail land-use, agricultural-input, harvesting, and transport burdens, whereas residues and industrial by-products can reduce some of these upstream impacts [3, 62, 63]. Thus, the environmental performance of vegetable tanning cannot be separated from the origin and processing history of the biomass used to produce the tanning extract.

7.3 The Heavy-Metal versus Organic-Load Dilemma

A major environmental distinction between chrome-containing and genuinely metal-free tanning systems concerns the nature of their waste streams. Chrome tanning can generate chromium-containing sludge and wastewater that require appropriate management because of the toxicological significance of chromium species [5]. By contrast, genuinely metal-free vegetable or organic tanning systems can reduce or eliminate intentionally introduced tanning metals, but may generate higher organic loads when tannin exhaustion is low [55, 56].

This distinction is important because a reduction in one pollutant class does not necessarily translate into an equivalent reduction in overall environmental impact. High concentrations of biodegradable or slowly degradable organic matter can increase oxygen demand and place additional pressure on biological wastewater-treatment systems. Consequently, improved exhaustion, reduced float, controlled dosing, liquor recycling, and appropriate wastewater treatment should accompany the transition to vegetable tanning [18, 55].

The treatment strategy may also be tailored to the effluent's composition. Microbial and enzymatic approaches can support the biological degradation or transformation of selected

contaminants [18, 19], while chemical treatment can be used when residual metals require targeted removal [20]. Phytoremediation and algal systems offer an additional pathway for pollutant removal and biomass generation [21]. This integrated approach aligns with the broader objective of moving from conventional end-of-pipe treatment towards resource-efficient and circular leather processing.

7.4 Comparative Life-Cycle Assessment Metrics: Global Warming Potential and Acidification

Global Warming Potential (GWP), acidification potential, eutrophication, energy demand, water consumption, and waste generation are among the indicators used to compare tanning systems. Existing LCA studies indicate that vegetable tanning does not automatically produce the lowest impact across all categories [12, 58]. Its environmental performance may be adversely affected when large quantities of biomass are cultivated specifically for tannin production, subjected to energy-intensive extraction, transported over long distances, or processed under conditions that involve prolonged tanning times.

Conversely, utilising locally available forestry residues and agricultural side-streams can improve the resource profile of vegetable tanning by converting low-value biomass into a functional tanning material. The techno-economic and LCA assessment of tannin production from spruce bark highlights the importance of integrating feedstock availability, extraction technology, process efficiency, and environmental indicators when assessing the industrial potential of waste-derived tannins [3]. Chemical modification and valorisation of tannin-rich biomass can further expand the potential uses of residues that would otherwise require disposal [62].

For this reason, comparisons of GWP or acidification potential should be presented as system-specific findings rather than as universal characteristics of vegetable or chrome-free tanning. Differences in functional unit, system boundary, electricity mix, biomass source, extraction method, transport distance, tanning formulation, and wastewater-treatment assumptions can substantially influence the resulting LCA profile [12, 58].

7.5 Land Use and Waste-Biomass Valorisation

One of the principal sustainability questions for large-scale vegetable tanning is the availability of tannin-rich biomass. Expanding dedicated tannin crops may compete for land and biomass resources, particularly where these resources have alternative food, feed, material, or energy uses [61]. A more circular strategy is therefore to prioritise residues and by-products from forestry and agriculture wherever their tannin content, availability, extraction economics, and chemical consistency are suitable.

Examples include bark and wood residues, agricultural processing wastes, fruit residues, and other tannin-containing side-streams. Such materials can deliver a dual environmental benefit by reducing disposal requirements and providing a renewable raw material for tanning. The circular-bioeconomy perspective emphasises that the sustainability of a biomass-based process depends not only on whether the material is renewable, but also on how efficiently the resource is recovered and whether its use creates additional competition for biomass resources [63].

Solid waste generated elsewhere in the tannery should likewise be incorporated into sustainability assessments. Onukak et al. [64] demonstrated the conversion of tannery solid waste into biomass briquettes, showing how waste streams can be redirected towards useful products rather than treated solely as disposal liabilities. More recent assessments of tannery solid-waste management further support the need for integrated strategies covering generation, recovery, treatment, and commercialisation [57].

7.6 Techno-Economic Considerations and Industrial Scalability

The economic feasibility of vegetable and chrome-free tanning depends on more than the price of the tanning extract. Key parameters include feedstock availability, tannin yield, extraction cost, energy demand, water consumption, tanning duration, chemical consumption, wastewater-treatment requirements, equipment modification, leather yield, and the market value of the resulting leather. Process intensification may reduce some of these burdens by shortening extraction or tanning times and improving tannin utilisation, but the economic benefit must be demonstrated at pilot and industrial scales.

For emerging feedstocks, local availability can confer a significant advantage by reducing transport and feedstock costs. However, variability in botanical composition, tannin concentration, seasonal availability, extraction yield, and non-tannin content may complicate industrial standardisation [2, 3]. Consequently, feedstock selection should balance chemical performance with supply-chain reliability.

The Nigerian context is particularly relevant because the transition towards sustainable leather manufacturing requires integrating technological development with institutional capacity, environmental management, research–industry collaboration, and policy support. Recent work on Nigeria's leather sector highlights the need for biophysical and biochemical innovation, cleaner processing technologies, improved waste management, and coordinated policy interventions to support industrial modernisation [65]. These considerations are directly relevant to the commercial adoption of locally sourced vegetable tannins and other chrome-free technologies.

From a public-health perspective, environmental management is also important beyond the factory boundary. Contaminated water, soil, and agricultural systems surrounding poorly managed tanneries may pose indirect risks to communities and food systems [67]. Sustainable tanning should therefore be assessed not only in terms of leather quality and factory-level emissions but also in terms of occupational, environmental, and downstream public-health implications [68, 69].

Overall, the environmental and economic sustainability of vegetable tanning is best understood as a systems problem. The most promising pathways combine renewable or waste-derived feedstocks with efficient extraction, improved tannin exhaustion, process intensification, responsible wastewater treatment, solid-waste valorisation, and LCA-informed process selection. Rather than assuming that vegetable tanning is inherently environmentally superior, future industrial development should identify formulations and supply chains that deliver demonstrable reductions in total environmental burden while meeting the performance and economic requirements of commercial leather production.

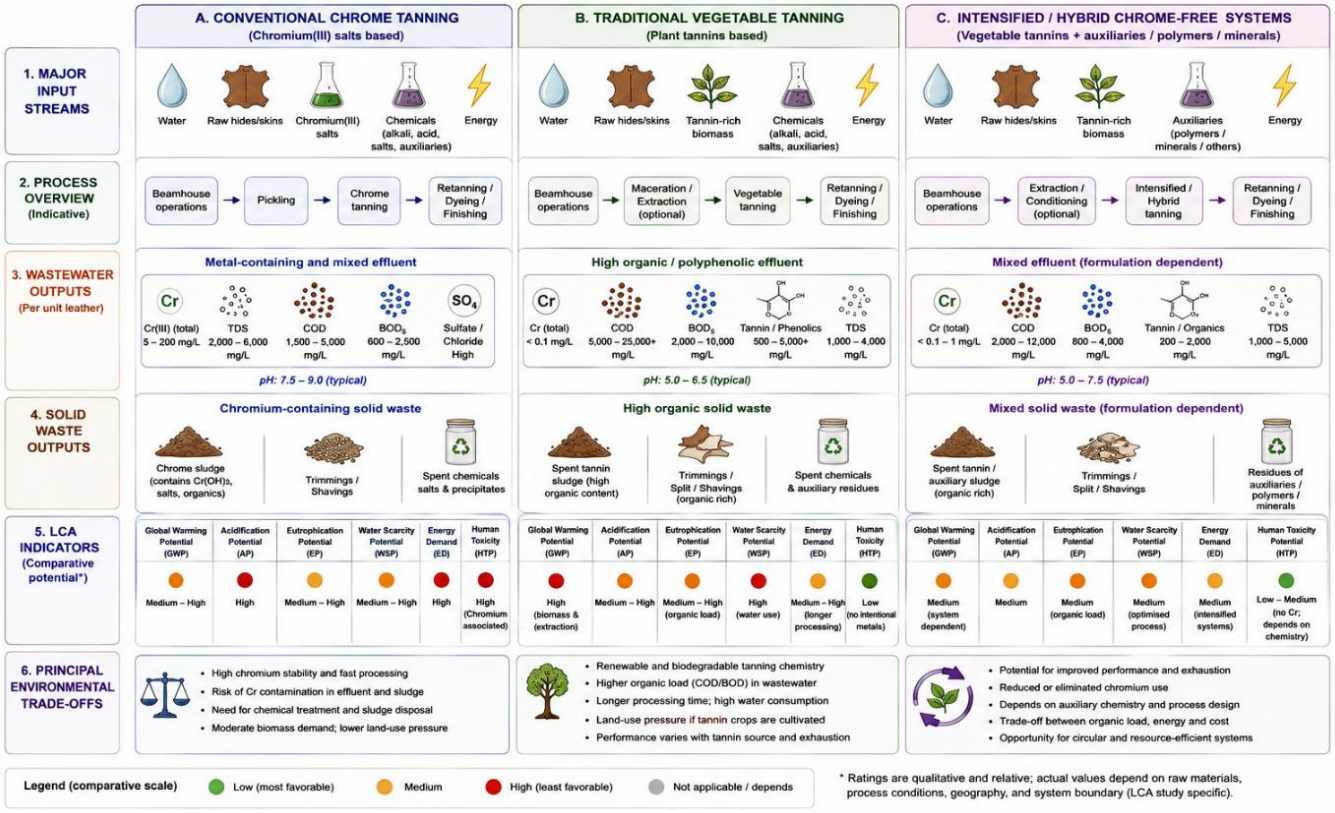


Figure 6. Comparative environmental assessment framework for conventional chrome tanning, traditional vegetable tanning, and intensified/hybrid chrome-free systems, showing major input streams, wastewater and solid-waste outputs, LCA indicators, and principal environmental trade-offs.

Table 6. Comparative environmental and techno-economic considerations for conventional chrome, vegetable, and emerging chrome-free tanning systems.

Parameter	Conventional chrome tanning	Traditional vegetable tanning	Intensified/hybrid chrome-free systems
Principal tanning chemistry	Chromium(III) salts	Plant tannins	Plant tannins + organic, polymeric, mineral or other auxiliaries depending on formulation
Major environmental concern	Chromium-containing wastewater/sludge	High organic loading and biomass/extraction burden	Formulation-dependent organic load, auxiliary chemicals and energy demand
Tannin/chemical exhaustion	Generally high for chromium salts	Often lower and dependent on tannin structure	Potentially improved through process optimisation
Wastewater profile	Metal-containing and inorganic/organic loads	Predominantly organic/polyphenolic load	Mixed and formulation-dependent
Wastewater treatment requirement	Metal and organic-load management	Strong biological/oxidative treatment may be required	Depends on auxiliary chemistry and residual organic load
Feedstock requirement	Mineral/chemical raw materials	Tannin-rich biomass	Tannin-rich biomass plus complementary agents
Land-use concern	Generally low for tanning agent itself	Can be significant for dedicated tannin crops	Potentially reduced when waste-derived biomass is used
Circular-bioeconomy potential	Moderate through chromium recovery and waste management	High when residues/by-products are used	High when renewable feedstocks and recyclable auxiliaries are integrated
Main economic challenge	Chemical and waste-treatment costs	Feedstock, extraction and longer processing time	Cost and complexity of formulation/process optimisation
Key sustainability indicator	Chromium discharge and overall resource use	COD/BOD, biomass sourcing, energy and LCA	Combined environmental burden, performance and process economics
Industrial priority	Pollution control and efficient chrome use	Improved exhaustion, feedstock selection and process intensification	Optimised balance of leather performance, cost and environmental impact

8. Conclusions and Future Outlook

Vegetable tanning has evolved beyond its traditional use in heavy sole leather and artisanal products and is increasingly being investigated as a viable component of sustainable leather manufacturing. This review has shown that the potential of vegetable tanning depends on the combined selection of tannin chemistry, botanical feedstock, extraction technology, tanning conditions, and downstream environmental management. Established sources such as mimosa, chestnut, Tara, and quebracho remain important, while regional and underutilised resources, including *Acacia nilotica, Parkia biglobosa, Azadirachta indica*, and forestry residues such as spruce bark, offer opportunities for feedstock diversification and biomass valorisation [2, 3].

Process intensification through ultrasound, microwave-assisted extraction, improved liquor management, and enhanced tannin penetration offers promising approaches to addressing the traditionally long processing times and relatively low exhaustion associated with vegetable tanning. Similarly, hybrid and combination systems can improve hydrothermal stability and mechanical performance while reducing or eliminating chromium, depending on the formulation. However, chrome-free, metal-free, and bio-based tanning should not be regarded as interchangeable terms, and the environmental advantages of any system must be demonstrated through appropriate performance and life-cycle assessment rather than inferred solely from the absence of chromium [43, 47, 49, 54].

The review also highlights that environmental sustainability remains a process-wide challenge. Vegetable tanning can reduce chromium-related concerns but may generate substantial organic loads if tannin exhaustion is incomplete. Effective wastewater treatment, including biological, chemical, and phytoremediation approaches, therefore remains important [18–21]. Similarly, using agricultural and forestry side-streams can strengthen the circular-bioeconomy potential of vegetable tanning, provided that feedstock availability, extraction requirements, transport, and competing biomass uses are considered [3, 61–64].

Future research should therefore focus on three closely related priorities. First, standardised extraction and characterisation protocols are needed for emerging botanical materials to enable reliable comparisons of tannin content, tannin-to-non-tannin ratio, chemical composition, and tanning performance across studies. Second, pilot- and industrial-scale validation of intensified and hybrid systems is necessary to establish reproducibility, process economics, leather quality, water and energy requirements, and wastewater performance under realistic production conditions. Third, integrated LCA and techno-economic assessment should be applied from feedstock sourcing through extraction, tanning, wastewater treatment, and end-of-life management to identify genuinely advantageous process configurations [3, 12, 53].

Another future opportunity is applying digital technologies and artificial intelligence to monitor leather processing, assess environmental impacts, and predict toxicological risks. Such approaches could enable earlier identification of hazardous process conditions and improve decision-making as the industry adopts increasingly diverse tanning chemistries [66]. For Nigeria and other regions with substantial agricultural and forestry resources, integrating locally available tannin-rich biomass with cleaner processing, waste valorisation, and appropriate environmental controls could provide a pathway towards more resource-efficient leather production [65, 70].

In summary, the future of vegetable tanning is unlikely to depend on a single tannin source or tanning formulation. Rather, progress will stem from integrating suitable bio-based feedstocks, efficient extraction, process intensification, appropriate chrome-free or metal-free tanning chemistry, effective waste management, and evidence-based LCA. The principal challenge is now to translate promising laboratory and pilot-scale results into reproducible, economically viable, and environmentally demonstrable industrial processes.

Author Contributions

JSD and AOA contributed to the conceptualisation and study design. JSD, AOA, DOD, BH, and EPA contributed to the literature search, data collection, screening, and synthesis of relevant studies. JSD and AOA conducted the initial analysis and interpretation of the reviewed literature. JSD and AOA prepared the first draft of the manuscript. DOD, BH, EPA, and SIRO critically reviewed the manuscript and contributed to its revision and scientific improvement. SIRO contributed to supervision, project administration, and the overall critical review of the manuscript. All authors contributed to interpreting the findings, critically reviewed successive versions of the manuscript, and approved the final version for submission. All authors have read and approved the final version of the paper and its submission and have given consent for publication.

Declaration of Generative AI and AI-Assisted Technologies in Scientific Writing

An AI image-generation tool was used to create figures based on concepts and designs provided by AOA and DJS. Grammarly was used for English-language editing and proofreading, while QuillBot assisted with reference formatting. The authors take full responsibility for the content and integrity of the manuscript.

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Data Availability Statement

No new datasets were generated or analysed in this review. All information presented is drawn from the published literature cited in the manuscript.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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