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Anaerobic digestion of tannery sludge and tannery waste: a systematic review

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ABSTRACT

This review investigated the application of anaerobic digestion (AD) as a sustainable solution for managing waste generated by the leather industry and sludge from the treatment of tannery effluents. The novelty of this review is the classification and discussion of the application of AD for both sludge and solid tannery waste, either as mono- or co-digestion with other substrates. The review underscored the potential of AD as a sustainable management of tannery waste and sludge, highlighting the feasibility of AD application to address the environmental challenges of the tanning industry. The application of AD represents a promising perspective in the leather industry, due to the specific nature and the high production volumes of tannery waste and sludge. The review highlighted the impacts of tannery sludge and waste origin and characteristics on biogas yields and digestion performance. The review also indicated the limited experience on mono-digestion of tannery sludge and tannery waste, and the key challenges as process instability, the seasonal variability of feedstock and the potential inhibition due to the presence of heavy metals. Co-digestion with other substrates was identified as a promising approach to improve efficiency and yields, as well as an opportunity to stimulate the implementation of AD in the tannery sector. The experiences on AD of tannery sludge and waste remain largely at laboratory scale, and this can hinder the scale-up of applications. The review discussed the research which made substantial contributions in this area and examined the treatment opportunities for a better understanding of the topic.

KEYWORDS

Tannery waste, Tannery sludge, Anaerobic digestion, Renewable energy, Circular Economy.

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1. Introduction

The role of the leather industry is important in the global economy. In 2022, the leather goods market size was valued at more than two hundred billion dollars, and further growth is expected on a global scale[1]. Leather is a unique, durable, and flexible material that provides a wide range of consumer goods by processing the hides and skins of animals, a waste product of the food industry[2]. Nonetheless, the tanning industry is known to negatively impact the environment mainly due to the large volumes of water demand, the high quantities of solid, liquid, and gaseous waste production, and the use of various chemicals (*e.g.*, hexavalent chromium) which are hazardous to humans, ecosystems and the environment. Moreover, the sustainability of this industry is highly weakened by a significant contribution to deforestation and greenhouse gas emissions associated with intensive animal farming[3]. In 2023, UNIC, the Italian Tanners' Association and other Leather Naturally members estimated that for one square meter of leather, about 122 litres of water and 2.46 kilograms of chemicals are consumed. Wastewater results from the wet tanning phases, the production of steam, the washing and cleaning cycles, and the abatement and cooling systems. According to their 'Sustainability Report', about 1.83 kilograms of waste are produced per square meter of leather, 22% of which is sent to disposal. The majority of the tanning waste production is represented by tanning liquids with a value of 37.5%, and about 14.3% is constituted by sludge[4].

The amount and the chemical composition of tannery sludge and waste are extremely variable: they depend on the tanning technologies used, the type of processed leather (bovine, ovine, etc), the characteristics of the tannery wastewater and the sludge management procedures applied at treatment plants. The content of hazardous organic matter and heavy metals, particularly chromium, is among the primary concerns in sludge management[5].

Globally, tannery sludge is currently landfilled due to its limited treatment options[6]. The problems caused by the unsustainable management of tannery sludge and tannery solid waste have repercussions on multiple aspects, including the environment, public health, and the economy.

Sludge disposal also offers interesting contrasts. Although the tannery sludge is not regarded as hazardous in industrialised countries, the cost of dewatering and disposal represents about 40% of the operational costs that treatment plants incur, as compared to only about 5% in India. With more stringent norms for organic content and recovery of valuable by-products from sludge expected soon, these costs will escalate further.

Sludge dewatering and final disposal account for 28% and 34% of the total cost of wastewater treatment plants in France and Italy, respectively. With more stringent regulations regarding organic content and the recovery of valuable by-products, these costs may rise in the future[7]. Tannery sludge can be dried as an option to reduce the volume for disposal, but this is an energy-intensive process, typically carried out by using fossil fuels such as natural gas. Drying can lead to risks of sludge self-combustion[8]; therefore, transport and storage are subject to strict regulations. Landfills are not a sustainable option for tannery waste and sludge due to the lack of proper sites, the production of unpleasant odours, and the problem of the high content of organic matter in the tannery sludge[9]. The presence of hazardous chromium ions causes risks of leaching into soil, freshwater, and groundwater sources; moreover, the potential oxidation of chromium from

trivalent to hexavalent, Cr (VI), poses environmental and health risks as it is a well-known and very hazardous pollutant for the ecosystem, and human beings[10,11]; similarly, the accumulation of Cr (III) in the soil can lead to contamination of the food chain or represent a potential source of Cr (IV) if oxidised in the environment[12].

Alternatives to landfilling are considered in the scientific literature in an attempt to identify more sustainable solutions for the disposal of tannery sludge and waste. Research activities have been focusing on thermo-chemical processes such as incineration, pyrolysis and gasification, on the recovery of chromium, and the stabilisation of these materials for their use in agriculture or the building industry[12].

Thermo-chemical treatments of tannery sludges are processes at high temperatures, in air or controlled atmosphere, thus with the partial or absence of oxygen. The main processes are incineration and combustion, pyrolysis, and gasification. Incineration and combustion occur in an abundance of oxygen; the difference between the two lies in whether energy is recovered during the process. The main drawback of these two processes is the risk of oxidation of trivalent chromium into hexavalent chromium, the potential NO_X and SO_2 emissions[13], and the possible leaching of heavy metals and chromium from the ashes[14]. Pyrolysis and gasification are more complex processes, with the main difference being that pyrolysis occurs in the absence of oxygen, while gasification takes place with a sub-stoichiometric amount of oxygen. These processes have great potential since they allow an efficient reduction of the sludge volume, they lower the emission of hazardous gases, if compared to combustion, and they produce energy as heat or syngas and fuel as bio-oil. The main drawbacks of these technologies are the high costs of processes, the lack of experience on large-scale installations applied to sludge, the availability of limited experiences at relatively small scales, the absence of political drivers or economic incentives for the development of these technologies, and the potential leaching of heavy metals from residual solid materials, tar, and char[15]. Recovery of chromium is another alternative for tanning sludge valorisation, but despite being an established technology, its drawbacks are the intensive chemical demand and the risk of secondary waste production with hazardous properties[14,16]. Other methods to recover value from tannery sludge are stabilisation in bricks for the building industry[17], use of sludge as an impermeable membrane filler[18], biological aerobic treatments for agricultural fertilisers or amendments, and recovery of lipids for biofuel[19].

All these different approaches are currently limited to either the laboratory scale or as pilot trials, and none represent an established solution for the management of tannery sludge and waste due to several drawbacks. To illustrate, the agricultural use of most potential products obtained from tanning sludge processing is highly restricted due to the possible leaching of chromium in the environment and potentially in the food chain[12]. Incineration can generate hazardous ash and, more importantly, induce the risk of chromium oxidation from Cr (III) to Cr (VI), which is hazardous to human health[20]. Other techniques, such as pyrolysis and gasification, are very expensive, and their environmental, social, and economic impact has not been thoroughly explored[21].

In this context, Anaerobic Digestion (AD) emerges as a biological, eco-compatible, and efficient alternative for tannery sludge management, allowing not only to obtain added value products, such as biogas, but also to

mitigate the environmental impacts of this waste by reducing its volume, offering a sustainable solution for waste management and renewable energy production[22–24]. Through a series of microbial processes, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis, anaerobic digestion transforms organic matter into biogas, predominantly composed of methane (CH_4) and carbon dioxide (CO_2)[25]. In recent years, there has been a notable surge in attention to the application of anaerobic digestion on tannery sludge and solid tannery waste, with a growing number of publications dedicated to these research areas (**Figure 1**). This raises a necessity for a systematic review to provide a comprehensive overview of the state-of-the-art.

A systematic approach has been applied to the discussion of the main topic: the anaerobic digestion of tannery sludge and solid waste. The core concepts of the research were identified in the following keywords: anaerobic digestion, tannery solid waste, and tannery sludge. The considered academic databases are Google Scholar, Scopus, and ScienceDirect. Figure 1 was built based on the analysis of available documents per year, referring to the Analyse search results of Scopus (anaerobic digestion AND tannery solid waste, anaerobic digestion AND tannery sludge) and is presented as cumulative values.

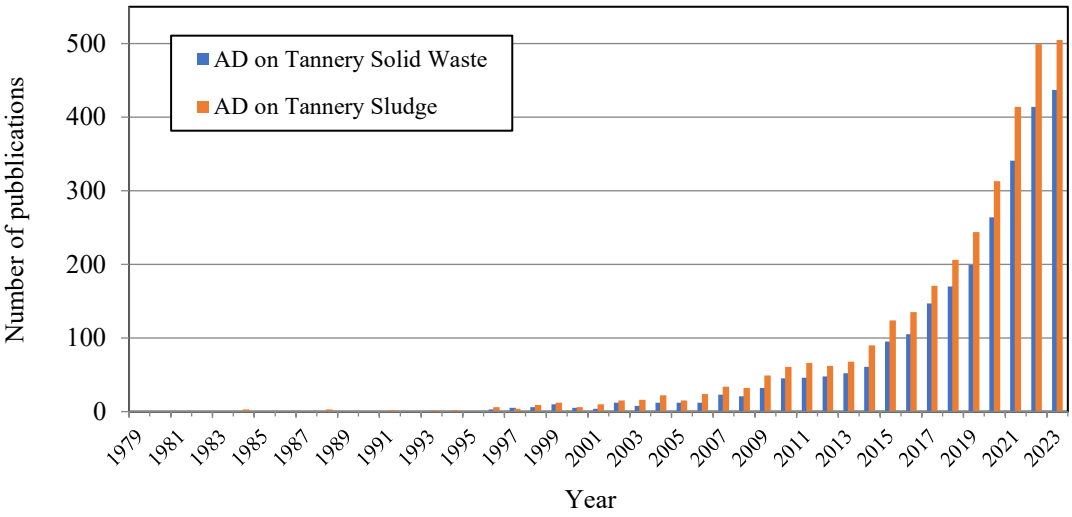


Figure 1. Cumulative number of publications in the area of anaerobic digestion of tannery sludge and tannery solid waste.

This work proposes a fresh eye approach to reviewing the current applications of anaerobic digestion to tannery sludge and tannery solid waste. To the best of our knowledge, only a few publications have currently reviewed this field, but provided only a broad overview of the options for tannery sludge waste management and did not include solid tannery waste[12,26]. On the contrary, this review aims to establish the current knowledge on the application of AD for tannery sludge and solid tannery waste, both in mono- and co-digestion with other substrates. Moreover, this review includes a discussion of the environmental and economic aspects of AD for tannery waste and a comprehensive analysis of the strengths, weaknesses, opportunities, and threats (SWOT) of AD for tannery residues to identify the critical bottlenecks and define the direction of new research in the field. The novelty and contribution to the knowledge of this review are the classifications of the available classes of tannery waste used in anaerobic processes, the comparison of

the economic and environmental impacts of the available studies, and the discussion of the potential for anaerobic digestion as a sustainable management solution for tannery waste and sludge.

2. Solid waste and sludge production from tanning activities

The production of finished leather results from a complex series of processes that generate significant amounts of various solid and liquid residues. Leather manufacturing also requires many kinds of chemicals, which are often discharged in wastewater and then found in sludge.

The tanning process (**Figure 2**) starts from the raw animal skin that has been stabilised by preparatory stages after the slaughtering of the animals[27].

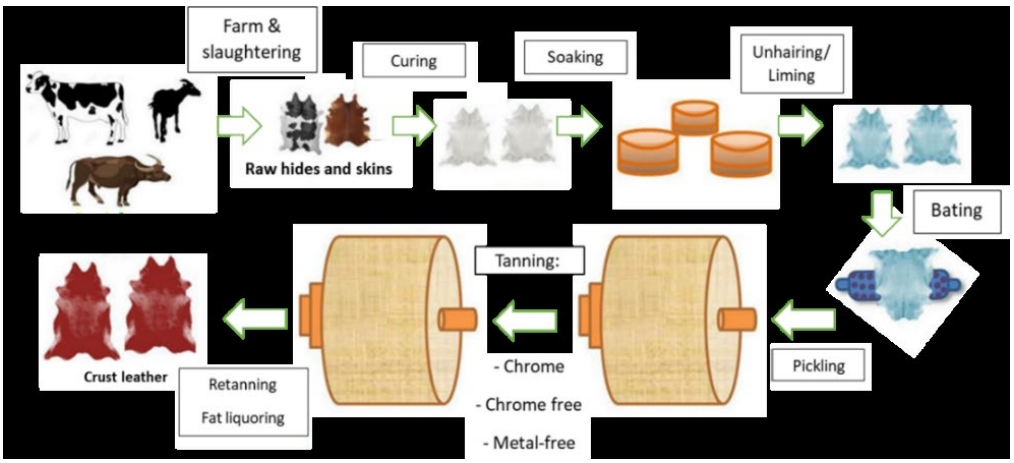


Figure 2. A schematic overview of the leather production process. Modified from [27]

Many of the leather manufacturing procedures are defined as 'wet processes', requiring water as an input. Water is necessary in different ways: it acts as a solvent for the hide-chemical reactions, softens the skin, and removes the residual chemicals. Thus, leather manufacturing is characterised by high water demand, and it correspondingly generates large volumes of waste. According to the type of tanning technology and the desired final product, one ton of raw hide consumes approximately 15 to 50 m^3 of water, about 500 kg of chemical products, and about 9.3 to 42 GJ of energy. The outputs of the tanning process include from 200 to 250 kg of finished leather, 15-50 m^3 of wastewater, 450 to 730 kg of untanned, tanned, and finished solid waste, from one to 10 kg of organic solvent emissions, and about 500 kg of sludge with a solid fraction of almost 40%[28]. For simplicity, the waste residues of the leather manufacturing process can be grouped into three categories: wastewater, gaseous emissions, and solid waste, which includes sludge. An estimation of the volume production and composition of the leather industry waste is represented in **Figure 3**.

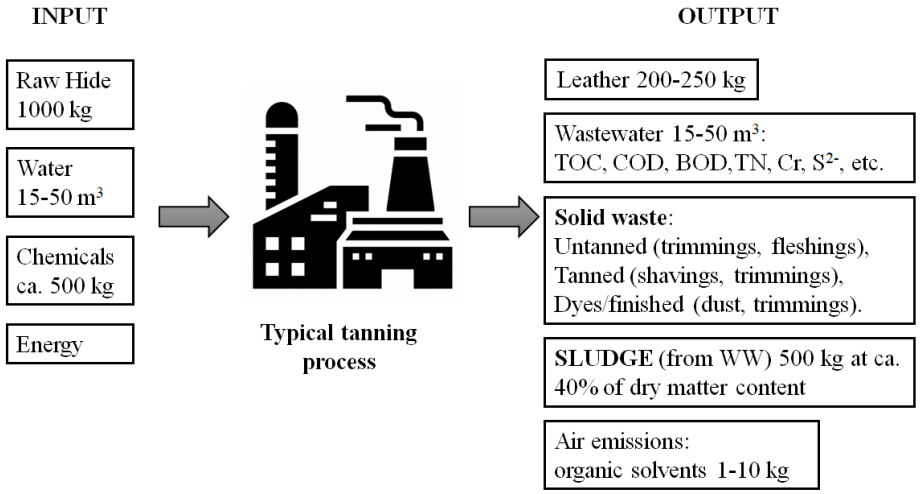


Figure 3. Liquid, solid, and emissions from finished leather production. Modified[28]

Because of the large quantity of chemicals, water, and the complex physical, biological, chemical, and mechanical processes involved in producing leather products, the amount of solid waste generated is among the most critical issues. The solid wastes are typically classified as untanned solid wastes, tanned solid wastes, and finishing wastes. The untanned solid wastes, as the raw trimmings and fleshings, are generated in the beam-house and pre-tanning processes. The tanned solid wastes, such as chrome shaving, tanned trimmings, and unusable splits, come from chrome tanning and re-tanning. The finishing wastes, such as buffing dust and dyed trimmings, come from finishing operations like conditioning, staking, milling, buffing, impregnation, coating, and polishing[29]. The primary use of these materials has been in the production of biomaterials, as it is characterised by high amounts of protein (30–35% collagen) and fat[30]. Despite the differences between different tanneries and tanning technologies, **Table 1** reports the percentage contribution to the generation of the different solid wastes of leather manufacturing[31].

Table 1. Percentage contribution of tanning solid waste. Adapted from [31]

Solid waste	Kg per ton of raw leather
Untanned trimming	120-150
Fleshings	70-230
Tanned splits	115-140
Chrome-tanned splitting and shaving	100-120
Buffing dust	2-5
Finishing trimmings	30-40

In European countries, including Italy and Spain, tannery wastewater and sludge are typically treated in tannery waste-specialised common effluent wastewater treatment (TCETP). The centralisation of these infrastructures represents an effective and sustainable way for the proper collection of solid waste and advanced practice for wastewater treatment practices, ensuring the protection of the environment and ecosystems, including humans, and respecting environmental legislations and regulations[32].

Tanning sludge is mainly produced from primary and secondary sedimentation tanks, respectively, after the physical-chemical and biological wastewater treatments. The primary sludge is mainly composed of settleable suspended solids that can be either easily degradable as collagen and proteins, or difficult to degrade, such as fibres and inorganic matter, including metal salts, carbonates, etc. Secondary sludge is composed of the settleable solids lost in the primary sedimentation and by the substances produced in the biological treatments (typically an activated sludge plant), including biomass residues, dissolved and suspended biodegraded matter, and non-biodegraded matter attached to the biomass[5, 30]. The chemical and physical properties of tannery sludge are determined by the nature of the treated wastewater and the technologies applied in the treatment plants[23,26].

Typical tannery sludge treatments aim primarily to reduce the volume, the amount of organic matter, and the number of disease-causing microorganisms present in the solids. Mainstream technologies and mechanisms for tannery sludge management are presented in **Figure 4**. Primary, secondary, and tertiary sludges coming from the respective wastewater treatment stages are first mixed in a homogenization tank to provide uniform particle size and chemical composition distribution. The thickening process aims to reduce the sludge volume by reducing the water content through physical treatments, including settling, flotation, or centrifugation. Conditioning is either chemical, by dosing inorganic coagulants and/or organic flocculants or thermal conditioning by heating the sludge under controlled conditions. This process aims to increase both the particle sedimentation rate and the permeability of the sludge. The stabilisation process aims to reduce the odour and putrescence of the sludge caused by the decay of organic compounds and to decrease the level of pathogenic organisms. It can be achieved either chemically, for example, with lime, or biologically with anaerobic treatments[29, 31]. The final conventional step of the sludge treatment in a common effluent treatment plant (CETP) is the dewatering process. The dehydration of tanning sludge aims to reduce the volume and weight of the sludge by partial separation of the liquid component. The process can be carried out mechanically by filtration or centrifugation, thermally, or in very limited cases, with natural methods of drying beds. The product thus obtained has a semi-solid consistency, which can reach 90% of solid content. Any liquids resulting from the dewatering stage are typically recirculated to the head of the wastewater treatment. The sludge is disposed of in landfills according to the regulations (Figure 4)[29, 31].

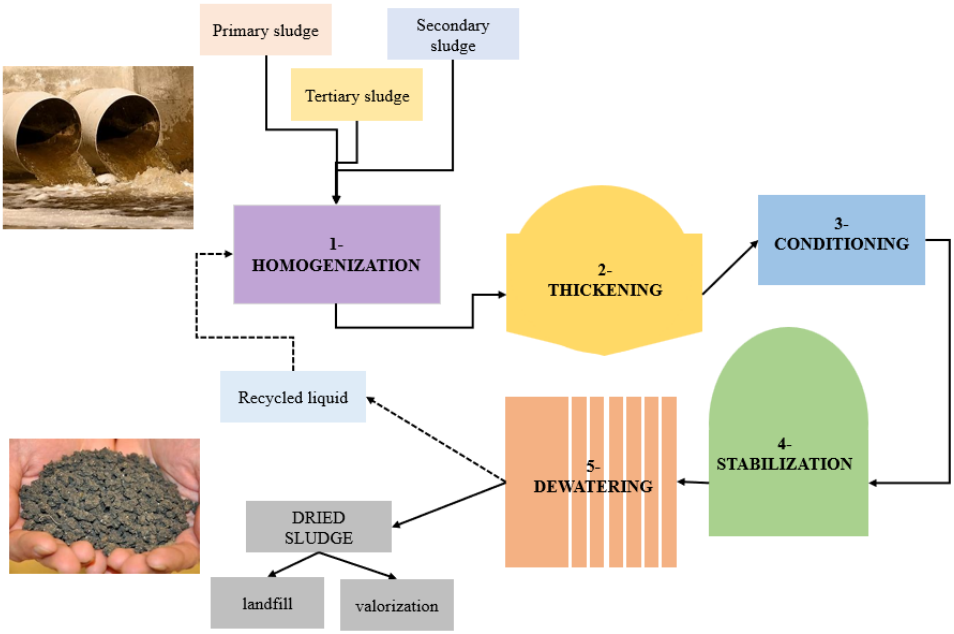


Figure 4. Example of tanning sludge treatment in TCETP

It has been estimated that around 90% of the global leather industry adopts trivalent chromium sulphate as a tanning agent due to its greater effect on the mechanical properties of the final product[33,34]. However, only approximately 30-40% of the added chromium in the leather processing is discharged, remaining in the wastewater effluent[23,35]. Primary physicochemical treatments can effectively remove dissolved trivalent chromium from effluent. Consequently, primary tannery sludge is often rich in precipitated chromium along with inorganic and organic compounds, classifying it as hazardous waste. The concentration of trivalent chromium has been measured at approximately 2.5% (w/w)[12] and around 500 mg/kg[36]. In addition to the organic content and water, which account for approximately 30% and 65%, respectively, tannery sludge is also rich in other hazardous materials, including sulphides and metals such as Calcium (Ca), Magnesium (Mg), Nickel (Ni), Zinc (Zn), Iron (Fe) [26, 34]. These compounds represent key issues for safe disposal and economical, environmentally friendly management. Despite the previous discussion, proposing a precise characterisation of tannery sludge is challenging due to numerous systematic bottlenecks:

1. Tannery processes significantly vary based on the final target products and the specific procedures and chemicals used by the producer.
2. The specific tanning and post-tanning procedures and agents can generally be divided into chrome, metal, and vegetable-based processes.
3. The parameters and procedures of the wastewater treatment plant are subject to seasonal and annual fluctuations.

However, different proposed characterisations are reported in **Table 2**.

Table 2: Composition of tannery sludge from literature. P = tannery sludge from primary sedimentation, S = tannery sludge from secondary treatments, P&S = tannery primary and waste activated sludge mixture, TS = tannery sludge

Parameter	[20]	[20]	[28]	[34]	[21]	[21]	[21]	[21]	[41]	[42]	[43]	[44]	[45]	[58]	[62]	[62]
Type	P	S	TS	P&S	TS	TS	TS	TS	TS	S	S	P&S	S	S	P	S
Total solids (%)	70.0	73.7	25-45	27	91	90.3	62.7	84.7		17.9	17.8	6.6		46.5	63.03	27.65
Organic matter (wt%)	57.7	72.9	40 – 75										36.87			
Volatile solids (wt%)	28.6	24.5	40-75		81.2	65.5	62.2	73.9	63	80.4	70	54.5		79.3	52.4	54.9
pH				8.2										8.2		
COD (% TS)					94.6	160.6	90.9	90.1		94.7 g/L	153				73.8	72.1
Sulphur (% TS)	2.0	1.4														
Fixed carbon (% TS)	18.0	39.2														
Carbon (% TS)	32.0	40.5														
Organic carbon (% TS)			21 - 38	42	12	29.4	18.0	3.7	20.4				21.44			
Ammonium (% TS)			0.1 – 1.6	2.6						262	0.28		0.06			
Organic nitrogen (% TS)			1.3 - 7													
TKN (% TS)				7.3					1079 mg/L				1.42	3.8	0.07	0.07
Total Nitrogen (% TS)					1.9	5.0	0.75	0.95		1780*	2880	140-200				
Total Phosphorous (% TS)			0.01 – 0.06	0.38	0.89	0.13	0.14	0.01		74.1*	86.2					

Sulphate (% TS)			1.5	1.4	0.64	0.71					
Sulphide (% TS)			0.05	0.001	0.03	0.006					
Total sulphur (% TS)	0.7 - 7										
Chromium (III) (% TS)	0.8 - 5	4.4	<0.01	0.17	0.58	0.16	145	205	268	2.7	
Aluminium (% TS)	0.1 – 5										
Iron (% TS)	0.6 – 12										
Copper (% TS)		4.1									
Nickel (% TS)		2.4									
Zinc (% TS)		0.109									
Calcium (% TS)	1 - 15										

*mg/L

3. AD applied to tannery sludge and tannery waste

Anaerobic digestion (AD) has been proven to be an eco-friendly technology able to deal with tannery wastes by reducing their volume, preventing, and reducing pollution, meanwhile recovering biogas as a source of renewable energy. To date, various studies have been conducted for the treatment of tannery wastewater[37,38] and tannery solid waste[39,40], but relatively less effort has been made for the application of anaerobic digestion on tannery sludge generated from the treatment of tannery wastewater.

3.1 Mono-digestion of tannery sludge

When the anaerobic digestion process relies on a single feedstock, it is typically referred to as mono-digestion. While this approach can produce biogas and CH_4 for energy recovery, its efficacy heavily relies on factors such as the organic content of the feedstock, the inoculum-to-substrate (I:S) ratio, and the potential inhibitory effects of contaminants like chromium, chloride, and sulphate, in the case of tannery sludge. Various studies have examined the parameters that affect the overall feasibility of the AD process (**Table 3**).

An important focus was on the type of tannery sludge and its preparation, and how these aspects influence AD performance. To illustrate, Akyol and Demirel[41] used three different tannery sludges to measure the anaerobic digestion efficacy in the production of biogas and CH_4 as potential energy sources. The substrates, obtained from a wastewater treatment plant of a tannery located near Istanbul, Turkey, include raw sludge cake from the belt filter press unit and seed sludge masses produced in the anaerobic digesters that treat primary and secondary sludge. The anaerobic digestion was investigated using a mesophilic batch anaerobic digestion system, focusing on fundamental parameters, such as inoculum-to-substrate (I:S) ratios and solids content, which were varied to evaluate the maximum biogas and CH_4 yields. The highest biogas and CH_4 yields obtained were 172 mL biogas/g VS added, and 89 mL CH_4/g VS added within an I:S ratio of 1:10, and 1:2, respectively. The relatively low biogas and CH_4 yields could be attributed to the low organic content of raw sludge cake. Interestingly, chromium, chloride, and sulphate, traditionally considered potential inhibitors of the anaerobic process, were not found to influence the anaerobic process negatively. Similarly, Mpofu et al.[42] provided a low-cost solids reduction and biogas production alternative for tannery sludge, eliminating the requirement of heating energy, pH correction, and mixing costs. Fresh sludge was sampled from a secondary clarifier of a South African tannery wastewater treatment plant, provided by a conventional activated sludge process with the pre-treatment and primary treatment units. The inoculum was obtained from a laboratory anaerobic batch reactor. At optimum operating conditions, biogas yields were 200–217 mL biogas/g VS added with about 55% of CH_4. According to the results, the maximum decrease of the concentration of TS, VS and COD was 86.8%, 81%, and 50.5%, respectively. The authors further investigate the adjustment of parameters, including the I:S ratio, adjusted to 4, resulting in a cumulative biogas yield of 150 mL/g VS added, of which 84 mL/g VS added of CH_4, meaning an increase of yield equal to 56%[43].

Zupančič and Jemec[44] measured the anaerobic treatment efficiency of Slovenian tannery sludge by mixing the excess biomass from the wastewater treatment plant and the sludge settled in the primary sedimentation. The anaerobic digestion efficiency was measured as biochemical CH_4 potential assays. The resulting biogas and CH_4 production were respectively at 0.973 m^3/kg VS and 0.617 m^3/kg VS. Similarly, Abbas et al.[45] found that secondary clarifier sludge from Pakistan's Kasur treatment plant performed better than primary and lagoon sludges, with cumulative biogas yields of 70 mL from a mixture of 80 grams of tannery sludge and 20 grams of cow dung, as raw weight, over 40 days under mesophilic conditions at neutral pH. These findings highlight the importance of sludge origin and treatment in determining biogas productivity.

Another key focus in the literature is related to the optimisation of the operational parameters to maximise the biogas yields. In this context, Ruiz-Aguilar et al.[46] explored the use of electron acceptors such as nitrate, iron, and urea in sludge from a Mexican tannery that does not use chromium as a tanning agent, and they found that nitrate amendments increased biogas production in 25 days. Additionally, reactors with a carbon-to-nitrogen (C:N) ratio of 6.0 increased biogas production in just 9 days, underscoring the role of nutrient balance in enhancing digestion efficiency.

Concerns have frequently arisen regarding the inhibitory effects of metals, especially chromium, on the anaerobic digestion process. Priebe et al.[11] measured the biogas production of activated sludge from a tannery wastewater treatment plant in southern Brazil and noted that chromium formed highly stable complexes that resisted microbial hydrolysis. However, their analysis showed no evidence of Cr(VI) oxidation during digestion, and the process still achieved a maximum cumulative biogas of 405.34 mL/g VS added, and CH_4 yields of 189.42 mL CH_4/g VS added.

Meanwhile, low organic content and unsuitable feedstock composition emerged as challenges in several studies. For instance, the lack of biogas production in Ijaz et al.'s mono-digestion experiment[47] on pre-tanning waste sludge from Pakistan's Sialkot district emphasised the need for co-digestion or pre-treatment to enhance biodegradability. These results highlight the necessity of tackling substrate limitations to enhance biogas production yields. Another important aspect of this research is the integration of modelling tools, as shown by Polizzi et al.[48], whose work not only assessed the AD potential of primary sludge but also offered important insights into kinetic parameters and simulation models. These models act as powerful instruments for optimising reactor performance and guiding the design and management of anaerobic digestion systems, thereby enhancing the applicability of the findings to industrial-scale operations.

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Table 3. Main anaerobic digestion parameters and results of mono-digestion studies on tannery sludge

TS type	Location	Inoculum	T (°C)	pH	RT (d)	RV (mL)	Biogas yield (mL/gVS)	CH4 yield (mL/gVS)	CH4 concentration (%)	Ref.
Raw	Turkey	Seed sludge	37	7.4–7.8	47	1000	1	89	52	[41]
Primary	Turkey									[41]
Secondary	Turkey									[41]
Secondary	South Africa	Laboratory prepared TS 2°	35.5–37	6.5-6.6	up to 105	500	200–217		55	[42]
Secondary	South Africa	Acclimated microbial pre-digested cow manure	35	7.0-8.0	up to 106	-	150	84	56	[43]
Mixture of primary and secondary	Slovenia	TS 2° municipal WWTP	37	7	-	1160	97	61	63	[44]
Secondary	Brazil	TS	35	7	86	350	405.34	189.42	48	[11]
-	Pakistan	fresh cow dung	32-35	7.2	-	2500	0	0		[47]
pre-tanning - primary	Mexico	Granular sludge from a UASB digester treating tequila vinasses	32.5	7	-	6000		260		[48]

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From the analysis of the published research, it can be concluded that there is a very low number of studies that reported the efficiency in biogas and CH_4 production by considering mono-anaerobic digestion of tannery sludge, probably due to the low efficiency or the low and seasonal availability of the substrate. Most of these studies are focused on chromium-based tanning sludge without considering the possibility of using tannery sludge coming from different types of tanning processes, such as vegetable and chrome-free approaches that produce sludge with different properties, including the absence of chromium. Anaerobic treatments were applied mainly on lab-scale reactors, with scale-up analysis and economic feasibility assessments either missing or incomplete. However, these studies proved that biogas and CH_4 can be recovered from tannery sludge by mesophilic anaerobic digestion, with a temperature of about 35° C, and a neutral pH. Acclimated inoculum can help to mitigate the inhibition by NH_3, H_2S and metal concentrations. These works contribute to comparing different sources of anaerobic microorganisms that influence the quality of digestate and the need for prior treatments of substrates containing chromium. This information can contribute to the development of anaerobic processes of solid waste treatment in tanneries, guiding this industry in a sustainable and more technological direction in terms of solid waste treatment and disposal. While globally many AD plants utilise mono-digestion systems, the main drawbacks of mono-digestion methods are the risk of instability of the bioprocess, the seasonal-based feedstock availability, the potential inhibition due to the presence of high concentrations of heavy metals, and the low biogas yield. Easily biodegradable waste can lead to the rapid accumulation of high concentrations of volatile fatty acids (VFA) in the reactor, inhibiting methanogenic microorganisms. Additionally, high proteinaceous substrates can generate high concentrations of ammonia (NH_3), a potentially toxic compound for the anaerobic microorganisms, and sulphate-rich sludges can produce hydrogen sulphide (H_2S) [34]. Adjusting the pH, controlling the retention time, feeding the reactor intermittently, adopting micro-aeration, using two-stage anaerobic systems, or using microbial diversity to maintain high biomass are approaches that can help address these issues, but they can lead to higher operational costs and complexity[49–51].

3.2 Mono-digestion of tannery solid waste

In addition to tannery sludge, other solid wastes are generated by the tanning process, including chrome shavings, tanned trimmings, and splits, collectively known as leather solid biomass (**Table 4**). These wastes have been explored for AD processes despite their intrinsic resistance and stability imparted by the tanning process, which makes them less suitable for this technology. Despite these challenges, only a few studies have investigated the feasibility of biogas production from leather solid biomass through AD in mono-digestion; however, contradicting results have been reported. Most research has shown negative results proving the impracticality of employing these residues for biogas production. For example, Kavan Kumar and colleagues[52] found that leather fleshings were unsuitable for biogas production through mono-digestion in batches. Similarly, Fernández-Rodríguez et al.[53] reported that despite various pre-treatment methods, including hydrothermal carbonisation and thermal hydrolysis, no valuable biogas was produced from chrome-tanned and chromium-free leather shavings, highlighting the recalcitrant nature of these

materials. On the other hand, a few studies have obtained some biogas production from these residues with the appropriate inoculum addition. Zupančič and Jemec[44], performing in-batch biochemical CH4 potential assays with solid tannery waste inoculated with pre-digested sludge, found that trimmings had the best specific CH4 productivity (SMP) at 37°C with 0.377 m^3/kg VSS, while fleshings performed better at 55°C with an SMP of 0.649 m^3/kg VSS. Moreover, Gomes et al.[54] studied AD under mesophilic conditions in batch setups, finding that, with a S:I ratio of 1.5, gelatine exhibited the highest biogas formation potential, with a maximum of 596.2 ± 18.2 L/kg of organic dry matter after around 60 days. This was followed by extruded shavings (454.8 ± 29.4 L/kg) and untreated shavings (299.1 ± 6.3 L/kg), with extruded off-cuts showing the lowest yield (203.4 ± 3.5), highlighting the importance of pre-treatment for effective collagen decomposition and improved performance. In a follow-up study, Gomes et al.[55] compared extrusion and hydrothermal pre-treatment of chrome shavings, finding that extruded wastes yielded 3.8% higher biogas (460 mL/g VS) than hydrothermally pre-treated wastes (443 mL/g VS). Priebe et al.[11] tested animal protein (collagen) at different stages of chemical stabilisation, including untanned (hydrolysed collagen), tanned with minimal chromium content (hide powder), and wet-blue leather (chrome shavings). With nutrient solutions to aid microorganisms and three different inocula (sewage sludge, slaughterhouse sludge, and aerobic sludge), the study found that hide powder produced 399.52 mL of biogas/g VS with aerobic sludge as inoculum, while chrome shavings produced a maximum of 162.16 mL of biogas/g VS with slaughterhouse sludge as inoculum.

These studies collectively demonstrate that while it is possible to obtain biogas from leather solid biomass, the process faces significant difficulties and requires further optimisation. Due to these challenges, alternative treatments are often preferable, and in the context of anaerobic digestion, co-digestion with other substrates is recommended to improve efficiency and yield.

362 *Table 4. Main anaerobic digestion parameters and results of mono-digestion studies on tannery solid waste*

Sample type	Location	Inoculum	T (°C)	pH	Reactor volume (mL)	Biogas yield (mL/gVS)	CH4 yield (mL/gVS)	CH4 concentration (%)	Ref.
Trimmings	Slovenia	TS 2° municipal WWTP	37-55	7-7.5	1160	547	377		[44]
Fleshings	Slovenia	TS 2° municipal WWTP	37-55	7-7.5	1160	1074	649		[44]
Hide powder	Brazil	sewage sludge, slaughterhouse sludge, aerobic sludge	35	7	350	399.52		71.21	[11]
Chrome shavings	Brazil	sewage sludge, slaughterhouse sludge, aerobic sludge	35	7	350	162.16		73.68	[11]
Gelatin	Germany	Sludge municipal WWTP	37±2	7-8.5	65	596.2 ± 18.2	-		[54]
Shavings	Germany	Sludge municipal WWTP	37±2	7-8.5	65				[54]
Offcuts	Germany	Sludge municipal WWTP	37±2	7-8.5	65				[54]
Extruded shavings	Germany	Sludge municipal WWTP	37 ± 2	8-8.5	65	460		Up to 68	[55]
Chromium leather shavings	Germany	Sludge municipal WWTP	37 ± 2	8-8.5	65				[55]

363

3.3 Co-digestion of tannery sludge

Co-digestion, using multiple feedstocks, has the potential to overcome some of the previously mentioned limitations due to the synergy of co-substrates, allowing for better stability, enhanced digestibility, higher quality of co-digestate, and yield of biogas produced. Moreover, it can reduce the inhibitory effect of intermediatory compounds like VFA and free NH3, increasing the conversion rate from acidification to methanogenesis. The Main anaerobic digestion parameters and results of co-digestion studies are summarised in **Table 5**.

3.3.1 Co-digestion of tannery sludge with slaughterhouse waste and cow dung waste

Slaughterhouse waste and cow dung are among the most common biological wastes linked to the increasing population and demand for food industry products such as meat, livestock, and poultry. Slaughterhouse operations produce an important amount of organic waste, which is typically composed of a high content of suspended solids, liquid, and fat[56]. For example, a bovine slaughterhouse generates solid waste equal to about 27.5% of the animal's weight. The solid wastes from the slaughterhouses consist of vegetable matter and animal matter. The by-products are fat, skin, tissue, organs, intestinal contents, bone, and blood, specifically rumen 80 wt.%, dung/manure 12 wt.%, blood 5 wt.%, and others 3 wt.%[57]. This waste received little consideration in the biogas-generating process[57].

Abbas et al.[45] worked on the anaerobic digestion of waste-activated tannery sludge utilising cow dung as a co-substrate. The efficiency of co-digestion using tannery sludge to cow dung in a ratio of 30:70, and 70:30 was measured to enhance the cumulative biogas production from 70 mL to 208 mL, 481 mL in mesophilic conditions. Similarly, Vasudevan and Ravindran[58], using recycled biological tannery sludge obtained from a TCETP in Dindigul, India, reported that a 7:1 sludge-to-cow dung ratio yielded optimal results, including a CH4 content of 48.8% and a 27.4% volume reduction. The digested slurry also demonstrated potential as organic manure due to its high nitrogen, P_2O_5, and K_2O content, highlighting an added environmental benefit of nutrient recycling.

Other studies focused on the optimisation of the operational parameters, including I:S and the influence of inhibitory compounds. Mpofu et al.[43] demonstrated the feasibility of integrating tannery and slaughterhouse sludge in anaerobic co-digestion and the importance of the inoculum-to-substrate ratio on energy yield and biodegradability. The Logistic, Cone and modified Gompertz models were found to accurately fit the experimental data with an R^2 value higher than 99.8%. Co-digestion improved the process kinetics and performance, particularly achieving CH_4 yields of 156% and biodegradability of about 59.4–96.7%; the lag phase was reduced by 59.3%, and the retention time by 53.7%. However, higher I:S ratios required increased reactor capacity, resulting in higher operational costs. Some years later, Mpofu et al.[59] focused on the effect of sulphate concentrations in co-digestion systems involving chrome-based ostrich tannery sludge. They found that lower sulphate content and I:S ratios above 3 maximised methanogenic activity, reduced dried solids by nearly 49%, and allowed for water and elementary sulphur recovery, providing both energy and environmental benefits. The recovery of energy from tannery waste has been

another focal point. Ijaz et al.[47] explored the anaerobic treatment of industrial pre-tanning waste from Pakistan's Sialkot district, located in Punjab province, a famous location for leather manufacturing. The study concludes that with the appropriate pH and temperature (6.8 to 7.5, and 32-35 ºC) and an appropriate combination of waste and manure, biogas was produced in just 39 to 40 days. The maximum amount of biogas was measured to be up to 1623 ml/kg when equal proportions of manure and dried sludge were processed. The results depicted that about 473 ml of biogas was biosynthesised from 1kg of a sample comprising 25% pre-tanning waste and 75% manure.

Even if globally 90% of the leather makers are still using chrome-based tanning agents, due to the consolidated culture, better aesthetic quality, and mechanical performance, no studies have studied how the tannin-based tanning agents affect the anaerobic co-digestion biogas production.

3.3.2 Co-digestion of tannery sludge and fleshings

Leather fleshings consist of skin residue originating from the removal with sharp blades of the subcutaneous connective tissue and meat residue adhered to the animal hide during the pre-treatment in tannery industries. The content of leather fleshings includes various components, including subcutaneous tissue, flesh, and fat; this last content is about 4–18%, although it varies according to the type of animal, feeding, climate, and flaying method. Fleshings negatively impact water and soil. However, they are usually recycled in the food industry, cosmetic industry, agricultural compost, biogas, and biodiesel production[60].

Focusing on the composition and proportion of feedstock, Kanchinadham et al.[61] investigated the effect of organic load on the anaerobic co-digestion of tannery solid wastes based on fleshings, primary sludge (PS), and secondary sludge (SS), generated during the treatment of tannery wastewater in a semi-continuous mode. The reactors were operated for 300 days. The 6 reactors in a semi-continuous mode were fed with different volatile solids inputs. The VS load of 68 g measured the highest efficiency with biogas generation of 470 mL/g VS added; moreover, the VFA/alkalinity ratio was in the range of 0.206–0.714, and stable conditions. Similarly, Kameswari's group[62] investigated the optimal mix proportions of fleshings (F), primary sludge (PS), and secondary sludge (SS) from tannery wastewater. A ratio of F:PS:SS = 1.00:2.70:0.30, with a residence time of 45 days, produced the maximum biogas yield of 385 mL/g VS added.

Further refinement was made to tackle the economic feasibility of the process, addressing the rate-limiting step of hydrolysis by adding commercial-grade lipase[63]. This resulted in a 15% increase in biogas generation, a CH4 yield of 0.31 m^3/kg VS added, and a reduction in the digestion period from 42 to 29 days. Notably, these adjustments reduced reactor volume by 30%, offering significant capital and operational cost savings. Using crude enzymes extracted from biomass would further reduce the operating cost.

Kinetic modelling has proven valuable for understanding and optimising anaerobic digestion processes. Thangamani et al.[64] used a first-order kinetic model to describe the mesophilic anaerobic co-digestion of limed fleshings, animal tissue waste obtained in the preparatory stages of leather processing in a tannery and primary sludge from the tannery effluent treatment plant limed fleshings and primary sludge. Primary sludge, which acts as a source of various microorganisms required for digestion, was added as a diluent in the ratio

438 of 1:1, on a weight basis, to suspend the fleshing solids and to achieve suitable flowability in the feed
439 mixture. Their batch reactors, operated at different initial VS concentrations and with a retention time (RT)
440 of 8 weeks, achieved CH4 content ranging from 71% to 77% and specific gas production rates between
441 0.419 and 0.635 L/g VS added. The first-order kinetic model was found to be an adequate kinetic model to
442 describe the anaerobic co-digestion. Moreover, the results indicate that the primary constituents of the
443 volatile solids in the feed mixture are fats and proteins, which suggests that biodegradability is a key
444 advantage of this type of substrate. In a comparative study, Bayrakdar[65] compared the performances of
445 single and two-phase mesophilic anaerobic co-digestion using leather flashings and tannery sludge,
446 consisting of primary and secondary sludge, collected from an industrial zone located in Turkey.
447 The single-phase system had higher CH4 yields (0.46 m^3/kg VS added) but was inhibited by H_2S
448 accumulation. In contrast, the two-phase system mitigated sulphide-related issues but faced challenges with
449 hydrolysis reactor foaming, which impacted performance.
450 The highest efficiency achieved, 47% higher than the control, was in terms of CH4 gas produced after 72
451 days when the fleshings-to-sludge ratio of the feed mixture was 0.35:1 in terms of total solids. According to
452 the Gompertz model, CH4 production in the optimised two-phase system was 54% higher than in the control
453 reactor. In another study, Bayrakdar[66] studied the optimum leather fleshings loading by investigating four
454 identical batch reactors with different fleshings-tanning sludge ratios (0:1, 0.25:1, 0.35:1, 0.50:1, on a dry
455 basis) in terms of the contribution of gas production. The results confirmed the boosting in CH4 production
456 of lipid-containing substrates and the main issues of H_2S inhibition and VFA accumulation for what concerns
457 this co-digestion system. The modified Gompertz model was applied to the batch tests to determine the
458 kinetic constants: 0.35:1 was found to be an optimum leather fleshings and treatment sludge ratio due to the
459 enhancement of 54% in CH4 production potential concerning the control test.
460
461 **3.3.3 Co-digestion of tannery sludge and shavings**
462 Shavings consist of solid waste from the trimming and leather shaping process. One of the major
463 environmental and socio-sanitary problems of leather shaving is the presence of chromium. Research for new
464 sustainable solutions for the management of leather shaving is becoming one of the most important
465 challenges for the tanning industry[67,68].
466 Agustini et al.[69] evaluated the efficiency of the anaerobic co-digestion of chrome-based leather shavings
467 and the sludge obtained from tannery factories in Brazil and their respective WWTPs located close to Porto
468 Alegre. Sludge, also used as inoculum, was collected after the final leather processing was made using
469 chromium salts as a tanning agent. Moreover, the authors evaluate the enhancement of the anaerobic process
470 efficiency by adding cattle hair waste, which represents another potential waste of the leather industry,
471 microalgae cultivated in tannery effluent and commercial silicone. The average biogas production for the co-
472 digestion of sludge and leather shavings was 20.9 ml/g VS added. When microalgae, cattle hair, and
473 commercial silicone were included, the values were 43.3, 19.4, and 18.8 mL/g VS added, respectively. The
474 CH4 percentages for microalgae and cattle hair were 58.40% and 57.40%, respectively, while the experiment

with silicone showed a value similar to the control at 59.1%. The same research group[70] also focused on wet-blue shavings and tannery sludge to measure the effect of the co-substrate ratio on gas production. In this work, they also evaluated the statistical influence of storage conditions, and they report the collection, manipulation, and quantification of anaerobic microorganisms. Two different storage conditions of the sludge were compared: ambient and refrigeration. The two-way ANOVA method was performed to analyse the two variables considered: sludge storage condition (ambient and refrigerated) and time (from 10 to 110 days, at 10-day intervals). The results suggested that the sludge storage condition did not influence the amount of biogas but the quality of the produced biogas, such as the amount of CH_4. The ambient sludge storage condition, at room temperature and with contact with atmospheric oxygen, showed higher CH4 production. The authors assumed that the oxygen diffusion into the sludge did not prevent the formation of anaerobic areas, benefiting the anaerobes, regardless of the temperature variation. The mixed wet-blue shavings and sludge generated up to 17 mL of biogas and 10 mL of CH_4 per mL of residue in the tested conditions. In 2020, Agustini's group[71], by using similar co-substrates (chrome-based leather fleshings and tannery sludge), evaluated the efficiency of the anaerobic process by different microbial compositions. The highest performance in terms of bioCH4 production was related to the archaeal family *Methanosaetaceae* and bacterial order *Bacteroidales*. After 150 days, they produced 26.1 mL/g VS of biogas with 52% of CH_4. This work aimed to show that the microbial composition and their dominance are effective tools for manipulation, isolation, and inoculation of the microorganisms inside the bioreactors, and they are strictly correlated to the maximisation of CH4 production.

In the work of Ijaz et al.[47] fats, shavings, and dried sludge were chosen as co-substrates for mesophilic anaerobic digestion. The three industries belonged to the Sialkot district, located in Punjab province, famous for leather manufacturing. Sludge was collected from the existing pre-tanning waste. The study concludes that if pH and temperature are maintained respectively at 6.8 to 7.5 and 32-35 ºC, an appropriate combination of waste from tanneries along with manure can produce biogas in just 39 to 40 days. The maximum amount of biogas was measured to be up to 1623 ml/kg when equal proportions of manure and dried sludge were processed. The results depicted that about 473 ml of biogas was biosynthesised from 1kg of a sample comprising 25% pre-tanning waste and 75% manure.

Even if globally 90% of the leather makers are still using chrome-based tanning agents, due to the consolidated culture, better aesthetic quality and mechanical performance, few studies have studied how the tannin-based tanning agents affect the anaerobic co-digestion biogas production. Specifically, chromium and vegetable tannins are considered the main tanning agents used in leather manufacturing, but their presence can represent an inhibition for anaerobic digestion.

Moreover, Agustini et al.[72] studied the influence of the tanning agent in the co-digestion of leather shavings mixed with sludge. This work's novelty lies in comparing biogas and CH4 production with and without a tanning agent, as well as examining the influence of the tanning agent under varying organic loads and waste recalcitrance. Specifically, a low concentration of chromium in sludge and shavings is more suitable for anaerobic digestion gas production with respect to its absence: chromium content enhanced

about 3 times the biogas production with a CH4 content of about 55%. On the other hand, high concentrations of vegetable tannin (in shavings) produced 70% less CH4 than the control experiments performed without tannins. The presence of chromium showed a high reduction of organic matter and a great increase of inorganic matter; the chromium was proven to be significantly suitable for anaerobic digestion until the initial concentration of 7.6 mg/L of chromium in sludge and 16.4 mg/L of chromium in shaving, confirming that the concentrations of chromium in the residues were not inhibitory. The vegetable tannin acted as an inhibitory substance; the majority of the residue underwent hydrolysis, and only a small part was mineralised to CH4, increasing organic matter. The same research group[73] investigated in an orthogonal array the efficiency of mixtures of solid wastes from tanneries containing chromium and vegetable tannins, and they also evaluated how organic and inorganic load can influence anaerobic digestion. The co-substrates, leather shavings, were obtained from two factories, one using a tannin-based and the other a chrome-based tanning agent and sludge coming from the respective WWTP located near Porto Alegre, Brazil. The biogas and CH4 productivity in terms of VSS was assessed. On average, the chromium-containing sludge assays generated 19.6 ml of biogas/g VSS added and 8.15 ml of CH4/gVS added, 4.8% VS reduction, 60.4% BOD5 reduction, 55% TOC reduction, 67% IC increase and 54.6% TN increase. Moreover, they showed a great mineralisation of the residue concerning tannin-based experiments, which also proved to be toxic. Different from sludge, the origin of shavings was not significant in any parameter, but this probably led to the small concentration of residues in the assays.

532 *Table 5. Main anaerobic digestion parameters and results of co-digestion studies. P = tannery sludge from primary sedimentation, S = tannery sludge from secondary treatments, P&S = tannery*
533 *primary and waste activated sludge mixture, TS = tannery sludge*

TS type	Co-substrate	Reactor (mL)	T (°C)	TS to co-sub. ratio	Biogas	CH_4 (%)	Ref.
S	Cow dung	1000-buchner flasks	25-37	30:70	208 mL/80g mass (40 days)	-	[45]
TS lagoon	Cow dung	1000-buchner flasks	25-37	70:30	481 mL/80g mass (40 days)	-	[45]
TS	cow dung	150-batch digester	-	7:1	78.45 mV/sec (32 g mass, 24 days)	48.8	[58]
P&S	slaughter	500-borosilicate reactors	37	50:50	431 mL/gTVS	49.9	[43]
TS	manure	2500- borosilicate bottles	32-35	50:50	1623 mL/kg mass		[47]
P&S	fleshings	5000/10000 -borosilicate reactors	28	PS:SS:F = 2.7:0.3:1	470 mL/gVS_{add}	70.0	[61]
P&S	fleshings	-	-	PS:SS:F = 2.7:0.3:1	385 mL/gVS_{add}	69.9	[62]
P&S	fleshings	650-glass bottles	-	VS (PS:SS:F) = 4.5g.:0.5g:2.5g	448 mL/gVS_{add}	0.31*	[63]
P	Lime fleshings	serum bottles	-	PS:LF =1:1	635 mL/gVS_{add}	72-77	[64]
TS	fleshings	5000-glass digesters	36	F:TS 0.35:1	-	71	[65]
P&S	fleshings	1100-batch reactors	36	F:TS 0.35:1		20.88**	[66]
TS	shavings	300-bench-scale bioreactors	35	TS:SHA 25:1	19.4 mL/gVS (daily)	76.8	[69]
S	Wet-blue shavings	350-bench-scale bioreactors	35	AS:SHA 25:1	17 mL/mVS	58.8	[70]
TS	shavings	300- bench-scale bioreactors	35	TS:SHA 25:1	26.1 mL/gVSS (150 days)	52 (150 days)	[71]
TS beam house	Pickled shavings	300- bench-scale bioreactors	35	TS:SHA 25:1	0.8 mL/$gVSS_{add}$	38.83	[72]
TS Chrome					10.96 mL/$gVSS_{add}$	63.86	
TS beam house	Cr-shavings	300- bench-scale bioreactors	35	TS:SHA 25:1	6.46 mL/$gVSS_{add}$	61.47	[73]
TS Chrome	Cr-shavings				15.01 mL/$gVSS_{add}$	57.22	
TS beam house	Vegetable shavings				0.01 mL/$gVSS_{add}$	1.58	
TS Chrome	Vegetable shavings				8.27 mL/$gVSS_{add}$	57.57	
TS vegetable tanning	shavings vegetable tanning				-	1.0	
TS Chrome tanning	shavings vegetable tanning					54.5	
TS vegetable tanning	shavings Chrome tanning					23.6	
TS Chrome tanning	shavings Chrome tanning					61.8	

534 *m^3/kgVSSadd, **mL/gVS

4. Feasibility of tannery sludge co-digestion in pilot or semi-pilot scales

In tannery wastewater treatment plants, sludge management accounts for nearly 30-40% of the overall budget and 50-55% of the process and maintenance costs of tannery wastewater treatment plants[40]. Energy costs in the tanneries' effluent treatment plants can account for up to 60% of the total[7]. Tanning sludge anaerobic co-digestion proved to be an effective way to not only digest waste efficiently, reducing its volumes, and produce valuable material (VFAs), but also a good method to produce renewable thermal or electrical energy, significantly decreasing carbon emissions and producing biogas or CH_4. However, landfills or incineration are still the main techniques for disposing of sludge and waste. The anaerobic digestion process can provide a solution to the growing problem of waste management and energy demand. On the other hand, the feasibility of an anaerobic digestion plant for the mixture of various types of tanning waste is a bottleneck from an economic and political point of view, and more research on development from lab-scale to pilot or full-scale is needed to address these issues.

The inoculum-to-substrate ratio, which can be translated into an organic load for reactors, represents a key factor that affects not only the stability of the feed substrate and the methanogenic capacity but also the economic feasibility in terms of the performance of the overall anaerobic process. Thus, the I:S ratio is a fundamental parameter that influences the anaerobic process in terms of operating costs. Kameswari et al.[74] further studied the optimisation of the I:S on the performance of co-digestion of fleshings along with primary and secondary sludge generated in Chennai, India, during the treatment of tannery wastewater. The economic significance of the I:S ratio as related to the volume of the anaerobic digester and the potential benefit of bioenergy generated is further discussed. Input substrate of 7.5 g on a dry weight basis was composed of 2.5 g VS from fleshings, 4.5 g VS from the primary sludge, and 0.5 g VS from the secondary sludge, with a C:N ratio of 6.0 in all the reactors. An increase in biogas production was measured from 1087 to 2933 for I:S ratios equal to 0.25, 0.50, 0.67, 1.0, 1.5, 2.00, and 2.30. The increase of I:S from 1.0 to 2.3 led to 1.5–2.12%. A higher load of inoculum has no significant influence, furthermore leading to an increase in digester volume and thus economic costs. Beyond the optimum ratio of 1.0 resulted in an additional volume of 33, 67, and 87%, respectively, required for I:S ratios of 1.50, 2.0, and 2.30, and the net incremental benefit in terms of bio-energy generation is 1.57, 2.09, and 2.09% only. Below 1.0, for I:S equal to 0.667, 0.5, and 0.25, the reduction in reactor volume is 22, 33, and 50%, and the decrement in terms of bio-energy generation is 50.7, 53.8, and 62.1%. Hence, optimisation of the I/S ratio is not only beneficial for arriving at the reactor volume but also for maximising the benefits of bio-energy generation. However, it is worth mentioning that the I:S is mainly for lab-scale tests and not very relevant for full-scale plants unless we look at the organic loading rate of the reactor.

Another fundamental parameter is the nutrient availability for the digestion process. Simioni et al.[75] optimised the nutrient solution to enhance the efficiency of the leather shavings and sludge co-digestion. The results obtained by the optimisation of the nutrient solution composition and ratio were a reduction of 71% and 35% in electric and thermal energy consumption, proving the competitiveness of co-anaerobic digestion

against landfill disposal, suggesting the importance of nutrient composition, and proposing a future perspective in the utilisation of waste or other residues as a source.

Overall, the final aim is to upgrade the AD process from a laboratory to a pilot or a full-scale setup; this plays a central role in refining and optimising processes, technologies, and treatment methods. Arumugam[76] studied the anaerobic co-digestion of limed fleshings, solid waste and sludge coming from the effluent treatment in a two-phase digester on a semi-pilot scale. The two-phase system comprised two separate reactors for the acidogenic phase and methanogenic phase, which were continuously stirred tank-type reactors in series (CSTR), with a total volume of 4 and 10L, respectively. The two-phase process of the digestion system has been modelled using the adaptive neuro-fuzzy inference system (ANFIS) with HRT, pH and organic loading rate (OLR) as input parameters and cumulative gas production as output parameters. The acidogenic phase reactor was fed with a mixture of tannery solid and sludge wastes in the ratio of 1:1 by weight. The average cumulative CH_4 production rate was 0.31 m^3 CH_4/kg VS fed and 0.15 m^3 CH_4/kg VS added. Furthermore, Agustini et al.[77] focused on the scale-up, economic, and energetic evaluation of the co-digestion of mixtures of shavings and sludge from tanneries in laboratory and semi-pilot scales. A linear consistency appeared in cumulative biogas and CH4 production with a doubled biodegradation rate to a five-fold volume of treated waste. The reduction of TOC, electric, and thermal consumption of 70%, 6.8%, and 1.6% highlighted the environmental and economic benefits in terms of disposal and cost savings. Other authors focused on the simulation of the possible energy saving or biogas production of a full-scale setup, basing their calculations on average daily waste production in specific locations.

Kameswari et al.[78] presented a study on the economic effect of substrate ratios on the tannery waste co-digestion experiments using fleshings from an Indian tannery industry and the primary and secondary sludge generated during the treatment of tannery wastewater. Results showed that the average biogas generation with a mixed proportion of fleshings, primary and secondary sludge of 1.00:2.70:0.30 was 385 /g of VS. Based on the experiments, the total biogas generation per year was estimated at $24.92*10^6$ m^3, equivalent to $17.44 * 10^6$ m^3 of CH4 per year with a total processing capacity of 700,000 tons per year, corresponding to the average value for Indian tanneries. In addition, for total leather processed in India, bioenergy production and greenhouse gas emission reductions were estimated at $52.15 * 10^6$ kWh per year and $0.3 * 10^6$ tons of CO_2-eq per year, respectively. The research revealed the significant potential for the Indian tanning industry to gain advantages from utilising bioenergy and carbon credits within the clean development framework mechanism. In the study of Zupančič and Jemec[44], the co-digestion waste composition included waste fleshings, skin trimmings, and sludge. Waste fleshings were predominated by lipid content, containing 90–92% of fat and up to 7% protein, and nitrogen content was 1.0–1.3% of dry matter. Skin trimmings contain protein (70–80%) and up to 20% fat in dry matter, with a total nitrogen content of about 10–12% of dry matter. The research highlighted the efficiency of two techniques: conventional semi-continuous and, more recently, Anaerobic Sequencing Batch Reactors (ASBR). The sterilised and hydrolysed tannery waste was composed of 50% waste sludge, 40% waste fleshings, and 10% skin trimmings (percentages are relative to VS). The study calculated the possible amount of biogas-CH4 produced and the sizes of full-scale, based on

608 average daily waste production in the local Slovenian tannery. The local tannery was a medium-sized plant
609 with an annual production of approximately 5,000 tonnes of leather, a water consumption of 300,000 m^3 per
610 year, and a wastewater treatment plant of 70,000 PE (population equivalents) in size. In the semi-continuous
611 experiment, the total CH4 production was found to be 980,000 m^3/year with a digester size of 1700 m^3 and
612 VS output of 705 tons per year. In the ASBR experiment, the maximum CH_4 production per year was
613 1,120,000m^3 with a digester size of 2,100 m^3, an exchange volume of 32%, and a VS output of 444 tons per
614 year. It was observed that although the ASBR process yields better results in biogas production and VS
615 removal, it far exceeds the reactor volume commonly used in the conventional process. The authors
616 suggested the consideration of other properties, including additional buffer tanks, biogas yield, and
617 efficiency, to implement the process and calculate the economic benefits. However, the anaerobic digestion
618 of selected substrates was possible at 268 mg/L of chromium (VI) and 2650 mg/L of sodium, making tannery
619 wastes suitable for biogas production.
620
621 **5. Methods to enhance the efficiency of tannery sludge and tannery waste digestion**
622 Anaerobic digestion of tannery sludge, along with co-digestion of other tannery waste such as fleshings,
623 shaving, or slaughterhouse waste that belongs to the same manufacturing chain, has proven to be an efficient,
624 effective and environmentally sustainable remediation technique as well as a method for renewable energy
625 production. However, the main technical bottleneck of this process is the presence of complex floc
626 structures, hard cell walls, and large amounts of molecular organic matter in the sludge, which may hinder
627 the hydrolysis step[79]. Consequently, researchers have tried to overcome these issues by applying different
628 kinds of pre-treatment to sludge-based anaerobic digestion. In general, effective pre-treatment techniques are
629 focused on the acceleration of the sludge solubilisation to enhance the biodegradation degree of the organic
630 content, especially during hydrolysis. The pre-treatments can be divided into physical, mechanical, chemical,
631 thermal, and biological. **Table 6** reports some examples of sludge pre-treatment for the enhancement of
632 substrate solubilisation, reduction of HRT, and enhanced anaerobic digestion performance.
633 *Table 6. Pre-treatments for enhanced anaerobic digestion*

Type	Pre-treatments	Advantages	Disadvantages	Ref.
Physical	Ultrasonication	Enhanced efficiency of CH_4 yield; acceleration of the process, enhanced microbial diversity	Increase energy consumption, operational cost, and higher complexity of the process	[80]
	High-pressure homogenization	Enhanced solubilisation compared to chemical treatments, higher CH_4 yield, reduced odours, reduced digester volume	Lower sludge dewaterability, operational cost, and complexity of the process	[81]
	Microwave irradiation	Evolving technology, thermal and non-thermal effects, and industrial feasibility	Unrevealed mechanism, possible issues of economic feasibility	[82]
	Electro-kinetics disintegration	Increased CH_4 yield by enhancing the solubility of organic matter and solubilisation of complex organic molecules; decreased dewatering period, enhanced stability of digested sludge and oxidation of the aliphatic structures	Increased energy consumption, operational cost, and higher complexity of the process	[83]
	Ball milling	Improved properties of the digestive slurry, shortened lag phase and increased CH_4 yield, reduced stirring consumption	Decreased simplicity of the process	[84]

Thermal	Low-temperature pre-treatment	Low input, simplicity, energy saving	Inefficient for the destruction of recalcitrant matter in biomass, unclear mechanism, and higher release of Cr in the liquid fraction	[85,86]
	High-temperature pre-treatment	Effective on specific biomass	Energy cost to be evaluated	[87]
	Freeze-Thaw pre-treatment	Shortened lag phase	No significant improvement in CH_4 yield	[88]
Chemical	Alkali pre-treatment	Significant increase in COD and CH_4 yield	Increase in chemical use, decrease in the simplicity of the process	[89]
	Acids pre-treatment	Improved biogas production, promoted disintegration and solubilisation of sludge (proteins), and enrichment of functional microorganisms	Increase in chemical use, decrease in the simplicity of the process	[90]
	Oxidation pre-treatment	Mesophilic condition, higher CH_4 production and yield, cellulose and hemicelluloses converted at a high percentage	Increase in chemical use, decrease in the simplicity of the process	[91]
Biochemical	Enzyme-assisted pre-treatment, anaerobic or aerobic pre-treatment	Increase in CH_4 yield and production	Decrease the simplicity of the process and higher the operational cost	[92]

Kameswari et al.[93] presented the effects of various pre-treatment processes separately in primary and secondary tannery wastewater sludge. They evaluated the effect of ozonisation, sonication, hydrogen peroxide, alkaline, and alkaline thermal treatment to enhance the soluble chemical oxygen demand as parameters for higher anaerobic process efficiency. The results were expressed in terms of the enhancement of the soluble-to-total COD ratio of primary and secondary sludge as parameters of hydrolysis performance. For ozonisation pre-treatment from 15 minutes of processing time, the ratio of SCOD to TCOD was increased by 233% for primary sludge and for 5 minutes of processing time by 280% for secondary sludge. The ratio was higher in the case of secondary sludge due to the extracellular polymeric substances. For sonication pre-treatment, a processing time of 2 minutes increased by 166% for primary sludge, and with a processing time of 1 minute by 200% for secondary sludge. The pre-treatment with hydrogen peroxide for primary sludge with a dosage of 0.06 grams of H_2O_2 per gram of total solids was found to increase the soluble-to-total COD by 43.5% for primary sludge, and a dosage of 0.3 g H_2O_2/g total solids increased the ratio of secondary sludge by 29.6%. During the alkaline pre-treatment, in which the pH was measured at a value of 11 with the addition of sodium hydroxide, the ratio was increased respectively for primary and secondary sludge by 133% and 160%; by alkaline thermal pre-treatment, the respective ratio was further enhanced by 200% and 260%, respectively. The order of effectiveness of the considered pre-treatments is: ozonation > alkaline thermal treatment > sonication. From a sustainable point of view, it was also highlighted that the alkaline thermal treatment requires pH adjustment, chemical addition, and heating energy of the sludge, while ozonation and sonication do not. It was finally concluded that ozonation and sonication are the best options for the pre-treatment.

Vineetha Antony[94] aimed to reduce the organic fraction of tannery primary sludge, which is considered hazardous waste in India, by focusing their research on enhancing the hydrolysis rate of the sludge during anaerobic digestion. Various pre-treatments have been applied and compared, including autoclaving, thermal treatment, alkali treatment, and biological sulphate reduction. The primary tannery sludge was collected from

CETP and was characterised by high levels of chromium and organic content, making it unsuitable for disposal in secured landfills. In the control test, anaerobic digestion of the tannery primary sludge at 10% was conducted with no pre-treatment. Solids concentration gave the following results: 30.8% of soluble COD removal and 31.2% of volatile suspended solids (VSS) removal in 61 days of non-mixing conditions. The thermal pre-treatment was found to be the best: at a temperature of 170°C, for 60 minutes, anaerobic digestion was enhanced respectively by 46.4% and 48.7%, as soluble COD and VSS removals in 35 days. A further increase in the performance was measured with a pH value equal to 8 and a feed COD/VSS ratio equal to 1.5, further enhancing the thermal pre-treated anaerobic sludge digestion to the extent of approximately 50% removal of both SCOD and VSS within 28 days. Biological treatment with sulphate reduction, by the addition of Na_2SO_4, achieved the maximum VSS removal by 54.4% in 35 days, but no CH4 was produced due to the presence of sulphide as an inhibition substance. The results of this investigation are helpful for the design of a pilot-scale study offering an alternative to landfill disposal of the sludge and increasing the landfill's lifespan. The effect of thermal pre-treatment for the enhancement of anaerobic process efficiency was also studied by Zhai et al.[95], promoting VFA accumulation using waste tannery sludge collected in Hebei, China. A dual strategy was proposed to improve the resource utilisation efficiency of tannery sludge. The elemental content of C, N, O, H, and S of the samples was: for the sludge supernatant (SST) 27.63%, 3.45%, no oxygen was found, 3.59%, 8.43%, respectively; for sludge solid (SS) 10.91%, 0.29%, 38.82%, 1.69%, 0.46%, respectively. Sludge supernatant contains 69.6 mg/L soluble polysaccharide, 1143.3 mg/L soluble protein, 72.2 NH_3-N mg/L, total phosphorus equal to 4.6 mg/L, soluble COD 4049.8 mg/L, and an alkaline pH equal to 13.5. The results in terms of VFA and acetic acid per gram of soluble COD were measured and performed in thermophilic conditions, 50°C. Hydrogen peroxide is a well-known oxidising agent, significantly stronger than molecular oxygen and able to act on organic compounds directly or indirectly through OH free radicals produced by the breakdown of the oxygen–oxygen single bond. Microwave (MW) irradiation is a thermal pre-treatment characterised by rapid uniform heating and energy efficiency compared to the more costly traditional heating alternatives. Tuci et al.[96] provided a viable alternative to the wasteful disposal of tannery sludge in landfills using anaerobic digestion with a combination of pre-treatments. The efficiency of the anaerobic process was evaluated in terms of short-chain fatty acids (SCFA) production in the acidogenic fermentation step. SCFAs are products of great commercial interest, as they can be utilised in many industrial applications, including chemical, cosmetics, food, agricultural, and petrochemical industries, and many others[97]. The novelty of the work lies in the study of the effects of temperature, pH, total solids concentration, and the combined MW-H_2O_2 pre-treatment. The results of the batch tests revealed that under both mesophilic and thermophilic conditions, the combined pre-treatment yielded comparable results. The production of SCFAs in the mesophilic and thermophilic tests reached maximum values of 16,800–17,700 mg of SCFA-associated COD per litre in about two weeks, and 23,700–26,200 mg/L in three weeks, respectively. Lower performance was observed in control tests without pre-treatment, and no significant effect was linked to the varying initial volatile solids

The studies on biogas production for both tannery sludge and tannery waste are performed in either mesophilic or thermophilic conditions[98], with temperatures in the typical ranges applied in AD (30-37 °C or 50-55 °C), and there is limited experience on the performance at psychrophilic conditions[42]. Fernández-Rodríguez et al.[53] investigated the possibility of exploiting thermophilic conditions to improve the solubility of collagen-based polymers present in tanning waste that are recalcitrant to biological degradation. The results showed that thermophilic digestion conditions achieved a high level of solubilisation of organic matter in tannery waste, leading to biogas production potentials comparable to those obtained at mesophilic conditions but with the substrate pre-treated with a thermochemical hydrolysis step[53]. These results indicate the potential of thermophilic digestion as an effective treatment to enhance the value recovery from tannery waste and sludge and suggest the need for further investigations.

6. Strengths, weaknesses, opportunities and threats of anaerobic digestion of tannery sludge and waste

The anaerobic digestion of tannery waste and sludge is a potential candidate for delivering sustainable management of these residues from the leather industry and the related tannery waste and wastewater management sectors. The main strengths of the AD of tannery residues are represented by the large scientific and technical knowledge of the bioprocess and the diffused application of this technology to various types of substrates. The knowledge and experiences on AD can support the technological development still necessary to implement digestion plants in the tanning industry. Similarly, experiences in the management of substrates with similar characteristics (e.g., sewage sludge, slaughterhouse waste, agri-food industry) can provide solutions to overcome the challenges due to the intrinsic characteristics of tannery sludge. Another strength is the availability of AD reactor solutions at various scales. This supports the possibility of implementing AD technologies of various scales and meeting the specific requirements of the local tanning industry or waste management company.

Whilst the general knowledge on AD, the direct application to tannery waste and sludge remains mainly limited to laboratory or pilot scale are weakness for the sector. This lack of experience at full scale can limit confidence in investing in the technology, as finding solutions to unexpected problems might be too risky. Similarly, tannery sludge and waste are complex substrates that are subject to change due to seasonality in the production of leather and various treatments at the wastewater treatment site.

However, literature examples illustrate the ongoing efforts to translate the benefits of AD from research settings to practical applications within the tannery industry, demonstrating the feasibility of the process. The implementation of AD technology and its potential scaling up for tannery solid wastes has been investigated. In the study, a linear consistency in the scale-up of biogas production indicated the feasibility of transitioning from laboratory findings to industrial applications, with the potential for significant cost savings in energy consumption and waste disposal[99]. Additionally, a research project focused on a dynamic AD process plant for leather shavings was conducted on a semi-technical scale, representing a step towards the industrial implementation of AD for this specific waste stream[100].

Another area of research aimed at enhancing the recovery of value from tannery sludge and waste via AD is the manipulation of the microbial communities active in the biological process[101]. The potential of this approach is to augment the capability of the microbial communities to overcome inhibitory conditions like elevated concentrations of ammonia, sulphur compounds or chromium, or to increase the biodegradability of the substrates[102]. Despite this potential, research on microbiological approaches for tannery sludge and waste AD remains limited[70,71] and needs more attention in the future.

The management of digestate from AD of tannery sludge and waste also remains an aspect that can hinder the implementation of this treatment solution. Whilst digestate from the co-digestion of tannery waste and sludge was suggested for direct application in soils as a substitute for mineral fertiliser[103], the chemical composition and presence of metals can limit the exploitation of this route due to legislative constraints [34]. The large use of chromium as a tanning agent can affect not only the biological process but also the quality of the final digestate, requiring the need for co-digestion or mixing with other substrates to achieve concentrations below inhibitory or regulatory levels. In addition, the Cr-rich digestate (as effluent from AD) could still represent a material whose final destination is the landfill [34]. Managing chromium in the digestate from anaerobic digestion of tannery waste is necessary due to its potential environmental risks. Implementing chrome-free tanning processes can preferentially eliminate the substance from the waste stream and consequently from the digestate[104]. On the other hand, chromium recovery technologies directly applicable to tanneries can be adopted to recover unused chromium from wastewater and reuse it in the tanning process. Alkaline thermal hydrolysis is a potential method that allows for the recovery of chromium, which can then be reused, aligning with circular economy principles and preventing contamination[105]. Alternatively, pre-treatment can be applied for chromium removal to reduce its concentration in the digestate: chemical precipitation using agents like lime[106]; chelating agents[107] or advanced materials such as magnesium oxide nanoparticles to remove chromium from tannery wastewater by adsorption and precipitation[108]. Finally, de-chroming of the solid tannery waste can be applied before or even after anaerobic digestion using mild phosphoric acid hydrolysis[67]. As well as chromium, managing the sulphur during AD application on tannery waste is essential to prevent inhibition of the process and ensure a safe digestate. In literature, some strategies have been proposed: pre-treatment of the tannery wastewater by desulfurization technologies[109], sulphide removal by air or oxidant[110], or coagulation[111]. Alternatively, the optimisation of AD conditions, including the management of sulphate concentration, the pH, the Organic Loading Rate (OLR), and the inoculum-to-substrate ratio (ISR), may be an advantageous method to maintain the sulphate concentration below the inhibitory threshold[112]. Microaeration and addition of specific chemicals, like organic polysulfide, able to digest sulphur and related compounds, or iron salts able to precipitate sulphides, can be in-situ sulphide removal methods[113–115]. AD post-treatments may include the removal of hydrogen sulphide directly from the biogas using traditional metal, such as water, NaOH, or scrubbers, activated carbon or biofilters, or iron oxide pellets [112]. Finally, some AD processes applied to tannery waste were found to even facilitate the recovery of elemental sulphur as a byproduct[116]. Besides the effectiveness of the mentioned methods, the appropriate strategy for

inhibitory compounds strictly depends on the type of tannery waste; thus a continuous research on the topic is necessary.

Finally, the main weaknesses that hinder a comprehensive comparison of the previous research include:

- the lack of characterisation of raw materials and substrates, such as TS, VS, TKN, TP, Cr;
- the lack of complete information on technical and environmental conditions used during the anaerobic digestion, for example, HRT, substrate volume, co-substrate ratios, reactor volume, and inoculum;
- the lack of consistency in the units of measurement of experimental results; some works present total daily biogas production, while others report outcomes in terms of total volatile solids added, and some focus on the maximum value achieved.

Co-digestion represents an opportunity for tannery sludge and waste anaerobic treatment. Results from the literature demonstrated that it could enhance the potential for biogas and energy recovery, thus increasing volume reduction and minimising the impact of the challenging characteristics of some tannery waste (slow biodegradability, unbalanced nutrient content, presence of toxic compounds). According to these assumptions, the tanning industry can identify opportunities for trans-sector collaborations (e.g., with the farming industry and/or the slaughterhouse sector) to establish a common residue management strategy that can benefit from the synergies between the various substrates and available resources[69,117]. The digestion of tannery waste and tannery solid waste is also a bio-process that can be integrated with other processes to maximise the recovery of energy or resources. AD can deliver volume reduction and bioenergy recovery in the form of biogas, thus reducing the mass load to downstream processes (e.g., thermal processes) and containing capital and operational costs[118].

Anaerobic co-digestion for waste volume reduction and biogas production has shown numerous advantages compared to mono-digestion. Co-digestion can improve the nutrient and organic balance, enhance pH buffer capacity, often enhance the biogas production and digestion rate, and produce a high-quality digestate usable in agriculture as a bio-fertiliser. Thus, co-digestion also has environmental, socio-sanitary, and economic benefits due to shared equipment and easier feedstock handling. On one hand, using slaughterhouse waste represents a potential integration of tanneries and slaughterhouses as biorefineries that can promote sustainable economic development in developing countries. Moreover, the use of tannery waste, including leather fleshings and shavings, as a co-substrate represents a chance to implement a circular economy perspective. The main threat to the co-digestion of tannery waste and sludge is the regulatory framework for anaerobic digestion of waste and sludge. Despite the reported benefits, environmental legislation in some Countries prevents the co-digestion of sludge from wastewater treatment with solid waste. The possibility of overcoming this limitation can be achieved by identifying digestate final disposal routes to prevent the spread of pollutants in farmland devoted to food production for human consumption.

807 Table 7. Results of the SWOT analysis for anaerobic digestion (AD) of tannery sludge and waste.

Strengths	**Weaknesses**
Large scientific and technical knowledge on AD	Applications limited to lab or pilot-scale
AD is a diffuse and well-developed technology	Variability and complexity of tannery waste
AD plants are available at various scales	Presence of inhibitory compounds
Similarities with other types of waste or sludge	Lack of consistency in data reporting
Opportunities	**Threats**
Co-digestion with other substrates	Legislative constraints for co-digestion
Co-location of AD plants with other sectors	Strict quality standards for digestate disposal
Trans-sector collaboration	
Integration with other treatment processes	

808

809 ## 7. Conclusions

810 The anaerobic digestion of tannery sludge and tannery solid waste represents a sustainable solution for the
811 disposal of these challenging residues from the tanning industry.

812 While the principles and the challenges of tannery waste treatment by AD are individually recognised, the
813 novelty of this review resides in its specific and structured organisation of the literature concerning their
814 intersection. By employing a process-oriented structure (mono and co-digestion) and categorisation by waste
815 stream (tannery solid waste and sludge), this review aims to provide researchers and practitioners with a
816 significantly clearer and better understanding of the application of anaerobic digestion to tannery waste.
817 Furthermore, the discussion section offers a synthesised and insightful analysis of the specific challenges,
818 opportunities, and optimisation strategies unique to this application, thereby simplifying the identification of
819 effective solutions and future research directions in this field.

820 Discussion of the environmental and economic aspects of AD for tannery waste and a comprehensive
821 analysis of the strengths, weaknesses, opportunities and threats (SWOT) of AD for tannery residues
822 identified the key bottlenecks and defined the direction of new research in the field. The novelty and
823 contribution to the knowledge of this review include the classifications of the available types of tannery
824 waste used in anaerobic processes, the comparison of the economic and environmental impacts of the
825 available studies, and the discussion of the potential for anaerobic digestion as a sustainable management
826 solution for tannery waste and sludge.

827 The application of AD still presents limitations, including the presence of inhibitory substances, such as
828 chromium and sulphur, which may need further research efforts. Despite these limitations, the economic
829 feasibility and environmental benefits of this technology remain compelling. Biogas production can
830 significantly reduce operational costs and energy demand for tanneries; the reduction of waste volumes, the
831 mitigation of greenhouse gas emissions, and the potential production of fertiliser align with the main
832 principles of a circular economy, contributing to a more sustainable tanning process.

The current scientific literature identifies these residues as having biogas and CH_4 yields comparable to other substrates more commonly used in anaerobic digestion, but the lack of detailed characterisation, the regional and seasonal variability, as well as the variable content of toxic residues, limit the implementation of full-scale digestion schemes. Co-digestion with other substrates can overcome some of the intrinsic limitations of tannery residues, and the industry can benefit from synergies with other sectors, in particular stock farming and the slaughterhouse industry, but environmental legislation can present limitations, particularly to protect the human food chain from contamination from the disposal of digestate. Further research is still needed to identify the possibility of integrating tannery waste digestion with other treatment processes to maximise the recovery of resources and minimise the final disposal of residues. Future research efforts may focus on fine-tuning operating parameters and developing pre-treatment methods, especially for recalcitrant wastes such as chromium and its associated risks with contamination. Moreover, comprehensive economic and life cycle assessments, along with research into the implementation of real-world, long-term operational studies and co-digestion options, are necessary to ease the wider adoption of anaerobic digestion for achieving a more sustainable and circular economy within the leather processing sector.

CRediT author statement

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Data Availability

This is a review paper, so new data are not reported.

Disclosure statement

The authors report there are no competing interests to declare.

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