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Review

May 1,3,5-Triazine derivatives be the future of leather tanning? A critical review☆

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ABSTRACT

Leather is produced by a multi-step process among which the tanning phase is the most relevant, transforming animal skin collagen into a stable, non-putrescible material used to produce a variety of different goods, for the footwear, automotive, garments, and sports industry. Most of the leather produced today is tanned with chromium (III) salts or alternatively with aldehydes or synthetic tannins, generating high environmental concern. Over the years, high exhaustion tanning systems have been developed to reduce the environmental impact of chromium salts, which nevertheless do not avoid the use of metals. Chrome-free alternatives such as aldehydes and phenol based synthetic tannins, are suffering from Reach restrictions due to their toxicity. Thus, the need for environmentally benign and economically sustainable tanning agents is increasingly urgent.

In this review, the synthesis, use and tanning mechanism of a new class of tanning agents, 1,3,5-triazines derivatives, have been reported together with organoleptic, physical mechanical characteristics of tanned leather produced. Additionally environmental performance and economic data available for 1,3,5-triazines have been compared with those of a standard basic chromium sulphate tanning process, evidencing the high potentiality for sustainable, metal, aldehyde, and phenol free leather manufacturing.

1. Introduction

The leather industry, one of the oldest activities of mankind and probably the first example of circular economy, transforms hides into durable and valuable goods for the manufacturing of clothing, footwear, furniture, car interiors and other daily use objects (Joseph and Nithya, 2009; Rosu et al., 2018; Reich, 2015; Covington, 2009).

The tanning industry plays a significant role in the global economy, driven by factors such as improved living standards, and evolving fashion trends. The global leather market, valued at \$242.85 billion in 2022, is expected to grow at a compound annual growth rate (CAGR) of 6.6% from 2023 to 2030, due to the rising demand for comfortable, stylish leather goods (Grand view research, 2009). The European tanning industry is responsible for 17% of the worldwide leather market with a turnover of 48 billion Euros, 36.000 enterprises, employing around 435.000 people. Italy produces 67% of the European market share, with a turnover of almost 5 Mio€ in 2019 (Cotance, 2020) (Fig. 1).

Albeit its economic relevance and benefits deriving from the recovery and recycling of a byproduct of the meat industry, the leather industry has often been the object of negative campaigns due to its high environmental impact and consequences on human health. ((PETA, 2023) . The Sustainable Apparel Coalition's Higg Materials Sustainability Index gives most leathers an impact of 159 (compared with 98 for cotton and 44 for polyester), due to its high contribution to global warming, water consumption and pollution (SAC, 2020). It is widely assessed that wastewater discharged from tanneries pollutes the soil, water and air causing serious health problems, such as asthma, dermatitis, hepatic, and neurological disorders, including endocrine disruptors (ISPRA, 2023). This is a consequence of the high load of chemicals used during leather processing and especially in the tanning phase.

Nowadays over 85% of the leather produced worldwide is tanned with Cr(III) salts ("wet blue") due to its low cost, versatility of use, and high quality of the finished leather produced. Nevertheless, Cr(III) can oxidize to highly toxic and carcinogenic Cr(VI) species, in finished

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leather, wastewater and sludge, by manganese oxides or high pH levels, and in soils by mobile ligands mediators such as citric acid, diethylene triamine penta acetic acid and fulvic acid (Xiao et al., 2020; Monga et al., 2022). Thus, effluents must go to wastewater purification plants and leather scraps must be disposed of as hazardous waste (China et al., 2020; Hassan et al., 2023).

Approximately 5% of the industry has adopted cleaner technologies to reduce chromium salts consumption (such as high exhaustion chrome tanning protocols) (Cao et al., 2017; De Aquim et al., 2019; Qiang et al., 2016; Suresh et al., 2001; Zhang et al., 2016; Zhang et al., 2018; Zhu et al., 2020), or employing different metal salts (aluminium, titanium, zirconium salts) (Anggriyani et al., 2021; Chen et al., 2023; Crudu et al., 2014; Ding et al., 2022; Ding et al., 2023; Madhu et al., 2022; Zuriaga-Agustì et al., 2015), which are useful technologies but nevertheless are inadequate to eliminate the environmental impact and health issues deriving from the use of metals.

A remaining 10% of the leather market share, produces chrome-free tanned hides ("wet white"), prevalently employing aldehydes, synthetic or vegetable tannins which are often more expensive and difficult to use and produce leathers with lower physical mechanical characteristics compared to chrome. Moreover, the problem of health for the consumer and the environment remains both with aldehydes and many syntans, since toxic substances can be released from these leathers (Chiampo et al., 2023; Sabatini et al., 2023; Yi et al., 2020). This poses a serious problem to the industry in the choice of alternative metal-free and toxic-free tanning agents, fuelling the debate regarding the need to replace chromium. In fact, most of the industry is still inclined to believe that if Cr(III) tanning is adequately performed, *i.e.* with appropriate waste management so that no leaching of toxic chemicals occurs, it still remains the best and most reliable solution available at industrial level (China et al., 2020; Hassan et al., 2023).

It is nevertheless true that for those manufacturing areas, where specific regulations prohibit the use of chrome leather, the industry has been able to overcome technical problems finding solid solutions, achieving high quality products (Martins et al., 2018; Sartori et al., 2010; Shi et al., 2021; Yorgancioglu et al., 2021). An important driving force behind the push towards chrome-free tanning is the automotive industry, the biggest user of chrome-free leather. In 2000 a Directive came into force in the European Union (EU) requiring the automotive industry to achieve a reuse and recycle target respectively of 95% and 85% by January 2015 (European Commission, 2023a). Moreover, the directive prohibited the use of hazardous substances, such as lead, mercury, cadmium, and chromium (VI), in new vehicles. Thus, wet white has prevailed over wet blue in this specific manufacturing compartment. This is a clear example that regulative restrictions promote positive changes even before the technological solutions are available by the industry. Similarly, this is happening today for the plastic industry as a consequence of the zero-waste emission directive and the ONU Agenda , 2030 sustainable goals (Beghetto et al., 2023).

Within this panorama, 1,3,5-triazine derivatives are gaining increasing interest as alternative tanning agents for chrome, glutaraldehyde, phenol-free leather production, as testified by the conspicuous number of patents, literature work and new chemicals rapidly being commercialized by the industry (Beghetto, 2015a; Beghetto and Agostinis, 2017; Biyu et al., 2021; Biyu et al., 2022; Cui and Qiang, 2019; Gamarino and Trimarco, 2010; Guowei et al., 2022; Junlin, 2021; Xianglong et al., 2019; Yu et al., 2020b; Zancanaro et al., 2013). It is interesting to note that while metal tanning agents and high metal exhaustion systems have been widely reviewed elsewhere, triazines have been neglected, albeit their industrial interest and applications (Hassan et al., 2023; China et al., 2020; Sabatini et al., 2023).

Thus, in this review, alternative 1,3,5-triazine based metal, aldehyde and phenol-free tanning agents will be considered, describing their production processes, reaction mechanism, and physical mechanical characteristics of leather produced (Fig. 2).

Moreover, environmental impact (measured by COD, BOD_5, biodegradability of wastewater (BOD_5/COD), total solids (TS), total dissolved salts (TDS), total suspended solids (TSS), total dissolved chlorides (TDC)), exhaustion rate of tanning agent, and economic viability as compared to a standard chromium tanning process (CTP) with basic chromium sulphate (BCS) will also be reported. Scope of this review is to help the industry, but also policy makers, high fashion brands and consumers to orientate in a complex and sometimes contradictory landscape, for the development of environmentally sustainable tanning systems.

2. Methodology

A systematic research of existing literature was conducted to thoroughly analyse the current status of 1,3,5-triazine-based tanning agents that are devoid of metal, aldehyde, and phenol components, giving a critical evaluation, enabling new perspectives to emerge and knowledge enhancement (Snyder, 2019; Jia et al., 2020; Torraco, 2005). A comprehensive analysis of the literature regarding leather tanning was mapped using a combination of different keywords such as: "triazine", "1,3,5-triazine", "metal-free tanning", "chrome-free tanning", "glutaraldehyde-free tanning", "phenol-free tanning", "sustainable tanning", "improved tanning", "alternative tanning", "whet-white tanning", "sustainable syntan", "sustainable leather production", "green tanning", "combination tanning systems", "circular economy". Specifically, one or a combination of two keywords were chosen for the selection of the papers and only those published in English language on peer reviewed journals have been reported.

Research papers included in the review were collected through Web of Science Scopus, Google Scholar, ScienceDirect, ResearchGate, and were published between 2013 and 2023. In order to find the most updated data and regulations, we also searched websites of relevant organizations, such as ECHA (https://echa.europa.eu/it/), European commission portal (https://commission.europa.eu/index_en), and European Law portal (https://eur-lex.europa.eu/homepage.html?locale=en). The last search was performed in October 2023. Higher relevance has been given to articles reporting environmental impact and sustainability parameters compared to chrome tanning processes.

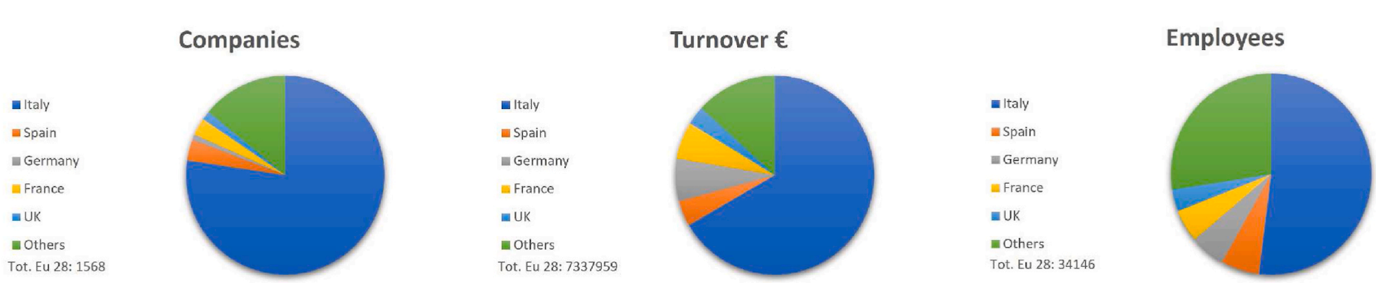


Fig. 1. The European tanning industry.

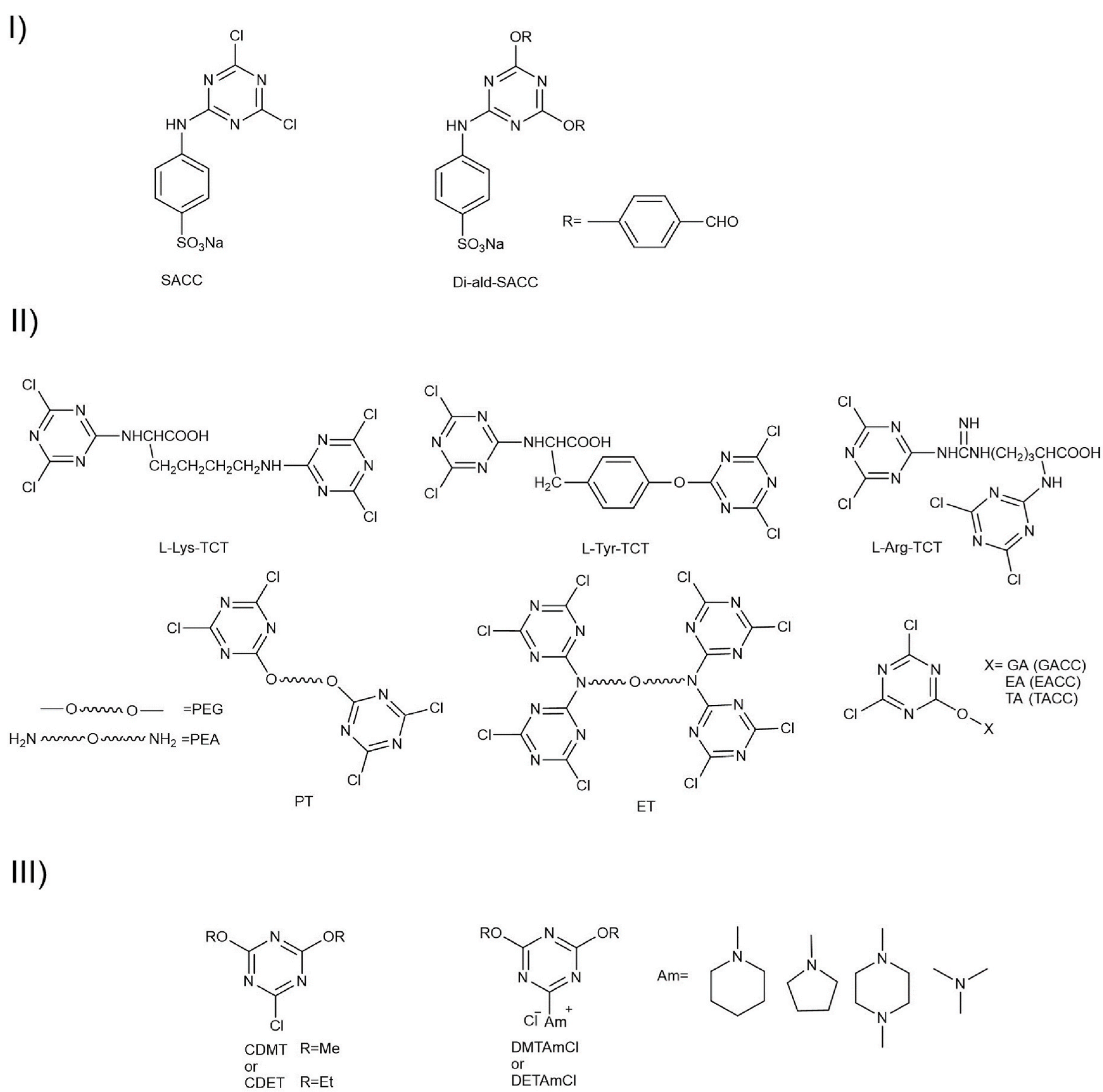


Fig. 2. Chemical structure of 1,3,5-triazine derivatives tanning agents reviewed in this work.

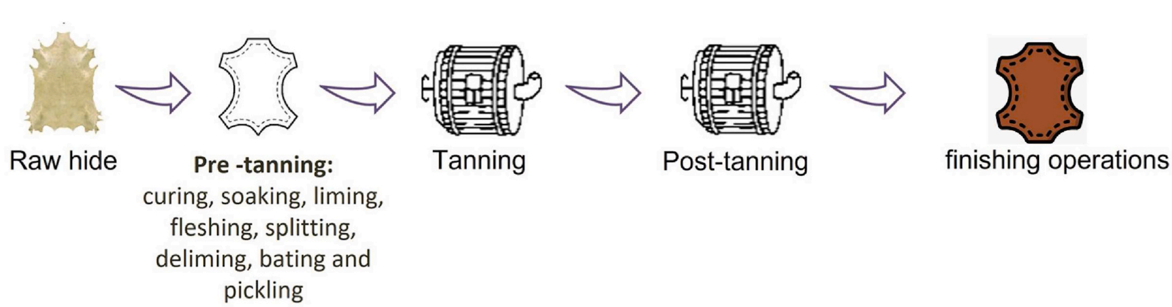
3. The leather industry

Leather and leather goods originate from the tanning of animal skins such as cattle, sheep, goats, and others (De Marchi and Di Maria, 2019; Jaegler, 2016; Covington, 2009).

In Europe, hides are mostly derived from bovine, ovine and caprine skins (Cotance, 2020). In Scheme 1 a general overall scheme of the main steps required to transform hides in leather is outlined (Kanagaraj et al., 2020).

Leather processing is divided into four main steps (i) pre-tanning or beamhouse operations during which skins are cleaned, degreased and dehaired; (ii) pickling and tanning transforming skin (collagen) from a putrescible into a stable matrix; (iii) wet end operations (retanning, dyeing and fattening) and iv) finishing operations, where aesthetic value is added (Covington, 2009).

Beamhouse operations are initially required to wash, degrease and



Scheme 1. General scheme of a tanning process.

dehair the hides which are then ready for the tanning step. After beamhouse operations, hides are mainly composed of collagen protein and water. Before tanning, hides are treated with an acid solution (pH between 2.5 – 5.0, pickling), in presence of sodium chloride, to allow the penetration of the tanning agent inside the collagen matrix of the hide. The pH of the acidic water solution (pickle float) is controlled to reduce the reactivity between the collagen protein and the tanning agent, allowing its effective penetration into the inner layers of the hide, then a base is added to promote the reaction between the tanning agent and collagen (Haroun and Ahmed, 2023; Covington, 2009; Laurenti et al., 2016). Overall pickling and subsequent basification increase the levels of Cl^- and SO_4^{2-} in wastewaters, posing serious problems in water depuration (Chowdhury et al., 2013; Chowdhury et al., 2015; Dixit et al., 2015; Giaccherini et al., 2017; Haroun and Ahmed, 2023; Humayra et al., 2023; Laurenti et al., 2016).

During the tanning step chemicals of different nature are added in variable quantities, between 5 and 40 wt% by weight of hide. Tanning agents are mainly divided into four categories, and specifically: i) metal salts (mainly chromium salts) (Bacardit et al., 2014; Madhan et al., 2003; Ollé et al., 2011), ii) aldehydes (mainly glutaraldehyde) (Chen et al., 2021; Han et al., 2003; Khor, 1997; Yi et al., 2020), iii) synthetic tannins (syntans) (Li et al., 2021; Fathima et al., 2011; Simon and Pizzi, 2003) and iv) vegetable tannins (Marsal et al., 2017; Adiguzel Zengin et al., 2012; Covington, 2009). Nature and strength of the bonds formed between the tanning agent and skin collagen depend on the chemical agent used. In particular, chromium salts form stable coordination complexes with the carboxylic groups of glutamic and aspartic acid present in the skin collagen protein, while aldehydes give covalent bonds between the pendant amine groups of arginine, lysine, and hydroxy lysine (Covington, 2009; Yu et al., 2020b; Beghetto et al., 2019a). Vegetable tannins give rise mainly to weaker hydrogen bonds between the phenolic-OH groups of the tannin and oxygen atoms or protonated amine groups present on the collagen protein (Bhavya et al., 2019).

Crosslinking generates an increase in the hydrothermal stability of skin collagen (Ts), corresponding to the temperature at which the leather sample suddenly contracts. Ts of native collagen is approximately of 45 – 50 °C, after tanning this value increases and higher values of Ts determine higher quality and processability (Beghetto et al., 2019b; Di et al., 2006; Onem et al., 2017; Scrivanti et al., 2018). To date the extraordinary supremacy of Cr(III) salts as tanning agents is mainly determined by the high Ts values achieved ($\geq$100 °C) notwithstanding its assessed environmental and health impact (Lofrano et al., 2013). Generally vegetable or syntans are rather inefficient tanning agents (Ts around 75–85 °C) (Onem et al., 2017; Covington, 2009), and are used by the industry mainly in combination with other tanning systems (aldehydes, metals, syntans) (China et al., 2020; Czirok et al., 2023; Haroun and Ahmed, 2023; Hassan et al., 2023; Oaishi et al., 2023; Zhora et al., 2023). As will be discussed below, 1,3,5-triazine derivatives form stable covalent bonds and give higher Ts values than wet white leather (ranging from 75 to 85 °C), and comparable to wet blue leather for many applications, as for example for the automotive industry (Beghetto et al., 2019a; Clariant Int Ltd et al., 2010). Tanned leather is further retanned, dyed and treated with different fattening agents to produce "crust leather" (Best Available Techniques, 2013).

4. EU regulations and restrictions affecting the leather industry

The leather industry poses concerning environment and health issues due to the use of high loads of chemicals, some of which of considerable hazard (Lofrano et al., 2013). Although in the EU there is no specific legislation, different regulations exist that have important implications on leather production.

For example, the environmental directive 2010/75/EU (European Commission, 2010) regarding integrated pollution prevention and control highly affected the leather market. According to this directive, tanneries must achieve authorizations from the competent authority stating the conformity of their activity, which should respect the principles of pollution prevention. To obtain this conformity, they can use and adopt Best Available Technologies (BAT) reported in BAT Reference Documents (BREFs).

Moreover, tannery operators should comply with Regulation EC No. 1069/2009 (European Commission, 2009), which lays down animal and public health rules for the collection, transport, storage, handling, processing, use or disposal of animal by-products. Additionally, EU regulatory framework on chemicals (European Parliament And The Council, 2006), places obligations not only on chemical manufacturers, but also on end users, i.e., tanneries.

Moreover, harmless Cr(III) may be oxidized during leather manufacturing operations to Cr(VI) which may cause severe damages to cellular membranes and health effects (China et al., 2020). Therefore, since May 2015, REACH Annex XVII restricts Cr(VI) in leather articles that come into contact with skin to a concentration of less than 3 mg/kg (0,0003 % by weight of leather).

Further, in the last years some of the most popular chemicals used as alternatives to Cr(III) salts have been restricted: formaldehyde for its carcinogenic activity, glutaraldehyde for its respiratory sensitising properties (REACH, 2015), together with one of the most common constituents of synthetic tannins, *p*-hydroxybenzene sulfonic acid (toxic to reproduction), 4,4′-isopropylidenediphenol (bisphenol A) and 4,4′-sulfonyldiphenol (bisphenol S) (endocrine disruptors for environmental organism).

It is thus evident that in view of the increasing restrictions imposed by regulatory actions throughout Europe and western nations, tanning agent selection criteria should be reconsidered, placing the requirement of the hydrothermal performance of tanned leather in a secondary, or equivalent position with respect to socio-environmental benefits. Considering that the tanning industry spends over 4% of its profits for waste remediation, it is possible that alternatives to chromium salts could also become economically sustainable in the long term (see below) (Beghetto et al., 2019a; Cui and Qiang, 2019; Wu et al., 2020; Xiao et al., 2023a).

In order to enhance EU competitiveness, prevent forgery and production delocalisation, the EU has put in place a huge number of different actions aiming to promote the adoption of safe and environmentally sustainable products and processes, in line with the UN ONU Agenda, 2030 (European Parliament and the Council, 2022; ONU Agenda, 2030). Among the tools which have been developed and are widely promoted by the EU commission, Life Cycle Assessment (LCA), Life Cycle Cost (LCC) and certifications derived (Ecolabel) are valuable instruments which allow to certify the quality, environmental and health safety of leather products (Bacardit et al., 2020; Ballus et al., 2023; Chowdhury et al., 2017; Conde et al., 2022; De Almeida et al., 2022; De Almeida et al., 2023; Kilic et al., 2023; Laurenti et al., 2016; Mahdi et al., 2021; Shan et al., 2019; Van Rensburg et al., 2020; Yang et al., 2021; Yu et al., 2021b).

5. Health issues of chrome based tanning agents versus triazine derivative

Although the leather industry uses harmless Cr(III), it can be oxidized to highly harmful Cr(VI) species, in finished leather, wastewater and slurries (Chandra Babu et al., 2005; Hedberg et al., 2014; Hedberg, 2020; Sharma et al., 2022). Cr (VI) pollution has become one of the world's most serious environmental concerns due to its long persistence in the environment and highly deadly nature in living organisms (Holmes et al., 2008; DesMarias and Costa, 2019; Moreira et al., 2019; Farrokhian et al., 2019; Peng and Yang, 2015; Speer and Wise, 2018; Wise et al., 2022). Cr (VI) is classified as a group 1 carcinogen by the World Health Organization (WHO) and by the International Agency for Research on Cancer (IARC) since it is known to increase the risk for several types of cancers and is also being recognized as a neurotoxicant (Wise et al., 2022).

Drinking water contaminated with Cr(VI) presents the most widespread risk of exposure, so average Cr(VI) levels in drinking water are regulated by law within a range of 0.2–2 μg Cr(VI)/L in different countries (US EPA, 2017; Moffat et al., 2018; GOV.IT,).

Cases of Cr(VI) detected in leather products have been reported by the European rapid alert system on dangerous consumer products (RAPEX). In fact, some of the chemicals used in post-tanning may lead to the oxidation of Cr(III) to Cr(VI) (Bayramoglu et al., 2012; Chandra Babu et al., 2005; Deselnicu, 2014; Yılmaz et al., 2016), which causes severe allergic contact dermatitis, respiratory issues, ulcers, kidney malfunction and even lung cancer (Angelucci et al., 2017; Bregnbak et al., 2015; Crudu et al., 2008; ECOPOL,; Hansen et al., 2003; Shi et al., 2016; Sharma et al., 2022). Additionally, Cr(VI) may be present in water effluents causing severe environmental and health issues (Apte et al., 2006; Başaran et al., 2008; Da Silva et al., 2011; Hedberg et al., 2018, Kumar et al., 2023). Additionally, exposure routes to Cr(VI) divided in two categories, occupational and non-occupational, has been extensively reported by China (China et al., 2020).

As far as 1,3,5-triazine derivatives reported in this work are concerned, it should be mentioned that this class of compounds are highly employed at industrial level for many different applications as for examples dyes (Benkhaya et al., 2020; Gao et al., 2023; Hoveizavi and Feiz, 2023; Patel et al., 2023), pesticides (Joo et al., 2010; Manousi et al., 2021; Velasco et al., 2021; Yao et al., 2023; Yu et al., 2021a), anti-cancer (Singh et al., 2021; Wróbel et al., 2020; Zou et al., 2023), anti-bacterial (Al-Zaydi et al., 2017; Green et al., 2022; Morandini et al., 2021a; Morandini et al., 2021b) and many other biological and pharmacological applications (Ali and Naseer, 2023). It should be underlined that this large variety of compounds shares the same core chemical structure but differ not only in application but also in their impacts on environmental, human, and animal health.

Although 1,3,5-triazines had been used in the past to tan leather (Heyden et al., 1959), only recently this class of tanning agents has been reconsidered (Beghetto et al., 2019a; Cui et al., 2017; Cui and Qiang, 2019; Facchin et al., 2017; Jia et al., 2022a; Li et al., 2021; Mikolaichuk et al., 2021; Wu et al., 2020; Xiao et al., 2020; Xiao et al., 2023a; Xianglong et al., 2019; Xu et al., 2021; Yu et al., 2020b). Consequently, fewer studies regarding toxicological and environmental impacts of 1,3,5-triazine derivatives as tanning agents are reported, compared to chromium or aldehyde-based tannins. Nevertheless, the few examples available are extremely important both from the toxicological and environmental point of view. Granofin F90®, for example, is classified by ECHA as a low hazard substance (ECHA, 2023a), with an LC50 value of 2000 mg/kg by both dermal contact and oral ingestion, compared to Cr(VI) that is classified as highly hazardous, with carcinogenic effects and an LD50 lower by two orders of magnitude (4 mg/L) (ECHA, 2023b; Morel et al., 2011). Again, 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) (Sole et al., 2021) is classified as Relatively harmless with an oral LD50 870 mg/kg (ECHA, 2023c), but in any case, much lower than Cr(VI). Moreover, CDMT is known to quickly decompose in water medium to form 2-hydro-4,6-dimethoxy-1,3,5-triazine which has very low environmental impact (Sole et al., 2021; Morandini et al., 2021b). Consequently, wastewater derived from the use of CDMT have modest to no environmental impact.

Additionally, Li recently reported a study on the effect of different 1,3,5-triazine compounds on the microbiological community structure in wastewater showing that these compounds have low impact in the proliferation of bacteria such as Pseudomonas, Clostridium and others which play a positive role in the removal of nitrogen (Li et al., 2021). According to the results reported by Li, 1,3,5-triazine derivatives tested are environmentally friendly tanning agents compared to chrome(III) salts.

6. Triazine based tanning agents

2,4,6-trichloro-1,3,5-triazine (TCT) is an important chemical product with low manufacturing cost and wide applications for the production of dyes (Gao et al., 2023; Hoveizavi and Feiz, 2023; Patel et al., 2023), catalysts (Sethiya et al., 2023), fine chemicals (Alshubramy et al., 2023; Banerjee et al., 2023; Beghetto et al., 2019b; Sole et al., 2021), condensation agents (Beghetto et al., 2020; Sole et al., 2020), antimicrobials (Morandini et al., 2021a; Morandini et al., 2021b) and water purification (Chen et al., 2023; Kharazi et al., 2023; Oprea and Voicu, 2023; Salahvarzi et al., 2023; Wang et al., 2023).

Nucleophilic substitution reaction of the three chlorine atoms in TCT takes place at increasing temperatures, between 0 and 5 °C the first, 25–60 °C the second, 80–90 °C the third (Gholap and Gunjal, 2017; Sharma et al., 2019; Xianglong et al., 2019). TCT derived compounds employed for leather tanning may be divided into three groups according to their chemical nature (Fig. 2) and will therefore be reported accordingly.

6.1. *Sodium p-((4,6-dichloro-1,3,5-triazin-2-yl)amino)benzene sulphonate (SACC) and 1,3,5-triazine derived*

In 2010 Clariant patented (Clariant Int Ltd et al., 2010) and soon after introduced Granofin® Easy White F-90, a tanning system mainly composed of sodium *p*-((4,6-dichloro-1,3,5-triazin-2-yl)amino)benzene sulphonate (SACC), produced by reaction of TCT and *p*-aminobenzenesulfonic acid (Fig. 2, I) (Xianglong et al., 2019).

According to Xianglong et al. the two chlorine atoms present in SACC react with the pendant amino groups of the collagen skin forming covalent crosslinking bonds, with a pickle-less process (pH 8.5–9.0) (Hollink et al., 2005; Wu et al., 2020) (Fig. 3a). Ts achieved in the presence of 4 wt% of SACC by weight of leather processed is around 78 °C, just slightly above the temperature required for further splitting and shaving (Ts > 75 °C). Although Ts are modest, main advantages of SACC are the low amount of tanning agent used and that no pickling is required. Among the main disadvantages are SACC's lo w solubility and reactivity. For this reason, temperature rise is required (from 30 °C to 80 °C) during tanning, making the process more complicated to manage since untanned or poorly tanned collagen skin may degrade at 45–50 °C.

To overcome some of the main problems encountered with SACC, Xiao et al. reported the use SACC in combination with tannic acid (TA) (Xiao et al., 2020). When a combination system is employed, the order of addition of the two chemicals is of great importance. Xiao in his work, in fact, reported that highest Ts (86 °C) were obtained when SACC was added before TA to the tanning bath. If TA was the first tanning agent used, Ts was lower (80 °C), while similar values of Ts (84 °C) were measured using SACC/TA together. This is probably a consequence of the strong filling effect of TA which, when used as first reactant, impedes penetration of SACC into the inner layers of skin collagen, reducing the tanning efficiency of the combination system. Additionally, Xiao et al. demonstrated that the advantage of adding SACC first derives also from the fact that one of the chlorine atoms of SACC rapidly hydrolysis in water solution leading to the formation of HCl, with a consequent pH drop from 7 to 5, promoting the reaction of the sulfonate group of SACC with the protonated amine groups of the collagen matrix (Xiao et al., 2023a). This in fact is also the main reason behind the possibility to use SACC devoid pickling.

Due to a synergic tanning effect, the combination of SACC and TA (Fig. 3b), leads to the formation of crosslinking bonds not only with the amine functional groups but also with carboxylic and hydroxyl functionalities present in the skin collagen. More precisely, according to Xiao a different hydrolysed SACC reacts with the pendant amino groups of Lysine, Hydroxylysine and Arginine, forming C–N covalent bonds. TA contributes to the tanning process forming additional crosslinking bonds between the protein and the NH_2 group of the benzene sulphonate molecule of SACC, contributing to enhance hydrothermal stability of tanned leather.

More recently Xiao et al. (2023a) reported an improved application of SACC in combination with various commercially available vegetable

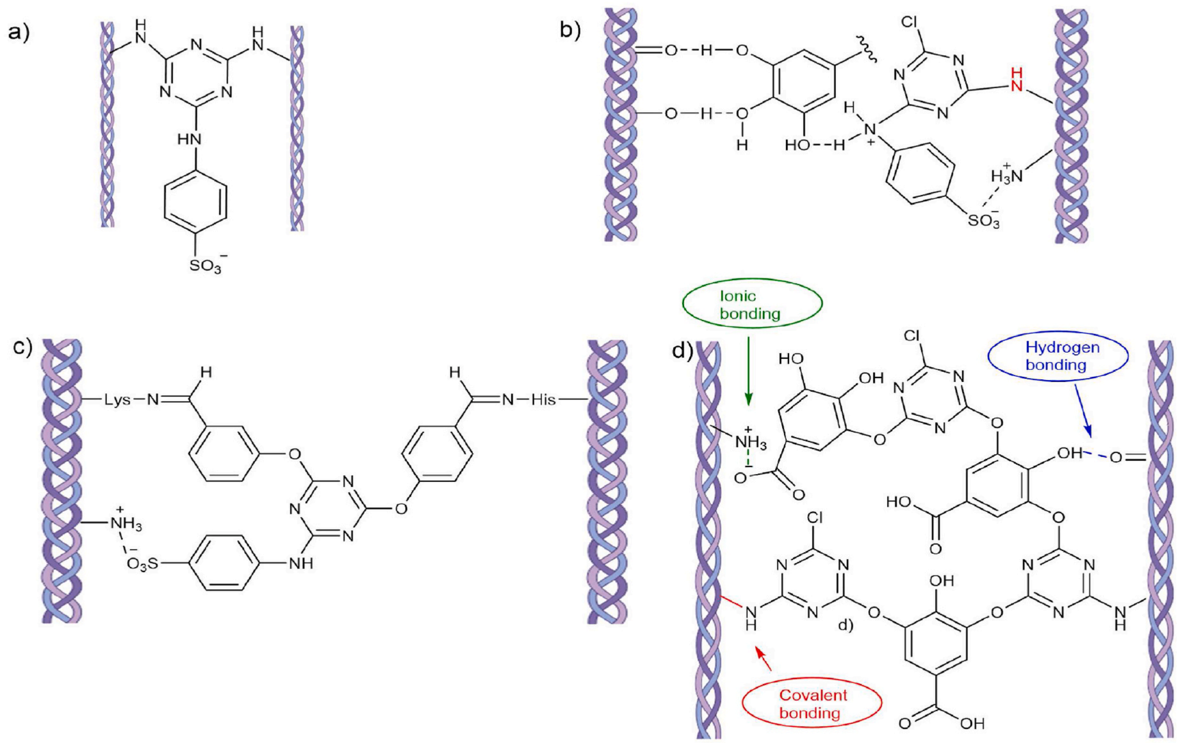


Fig. 3. Proposed interaction mechanism of a) SACC, b) SACC/TA, SACC/Vegetable tannins, c) Di-ald-SACC and d) triazine-conjugated polyphenols with collagen skin.

tannins both hydrolysable (*i.e.,* Chestnut, Valonia and Tara extracts) and condensed (*i.e.*, Wattle, Quebracho and Bayberry extracts). This strategy not only allowed to reduce further processing costs (TA is more expensive than conventional vegetable tannins) but also to improve tanning efficiency and quality of the leather (Table 1, section 7). The reaction mechanism reported for these SACC/vegetable tannins combination systems is the same as for SACC/TA (Fig. 3b). The Ts of leather tanned in the presence of SACC/condensed tannins (80–91.7 °C) was higher compared to hydrolysable tannins (75–80 °C), due to their stronger astringency (Endres, 1964; Falcao and Araujo, 2018).

Tanning experiments with SACC and these vegetable tannins were carried out analogously to SACC/TA. First 10 wt% SACC was added and

Table 1
Physical mechanical performances of leather tanned with BCS and different 1,3,5-triazine tanning agents.

Tanning agent	STD	BCS	SACC	SACC/ TA	SACC/ Wattle	Di-ald-SACC	L-Lys-TCT	PT	ET	GACC	DMTMM	CDET/ NMM	Upholstery leather
Hide		Cattle Crust	Goat Tanned	Goat Tanned	Cattle Crust [a]	Sheep Crust	Sheep Crust	Cattle Crust	Cattle Crust	Cattle Crust	Calf Crust	Calf Crust	
T_S (°C)		109.2 ± 0.2	77.3 ± 0.8	86.5 ± 0.7	91.9 ± 1.0	79 ± 4	82.5	80.8 ± 0.3	83.9 ± 0.2	77.0 ± 1.0	87 ± 1.0	82 ± 1.0	>75
Tensile strength (N/mm^2)	IUP 6	18.3 ± 0.1	13.8 ± 2.4			39[b]	16.2	15.3 ± 0.1	16.2 ± 0.0	12.0 ± 2.0	21.0 ± 0.5	20.0 ± 0.5	>8
Tear Strenght (N/mm)	IUP 8	40.2 ± 0.5	43.5 ± 3.9	45.4 ± 3.3				44.2	47.9 ± 0.2	59.0 ± 2.0	37.0 ± 0.3	36.5 ± 0.3	>20
Tearing load (N)			48.8 ± 3.1	52.2 ± 4.4	122.4 ± 7.2		37.7						≥40
Elongation at break (%)	IUP 6	46.0 ± 0.8	44.3 ± 2.1	58.3 ± 2.4		89 ± 3.0[c]		66.8 ± 0.2	100	58.0 ± 2.0	42.0 ± 1.0	44.5 ± 1.0	≤80
Elongation at 10 N (%)			21.8 ± 3.2	26.2 ± 4.1	37.9 ± 3.5		27.6		65.1 ± 0.3				≤40
Softness (mm)		8/10	4/5		6/10	8.5/10		8.6/10	8.8/10	5/10	7-9/10		
Fineness of grain		4/5				8.0/10		4/5	4/5		7-9/10		
Fullness		5/5				7.5/10		5/5	5/5		7-9/10		
Ref		Jia et al. (2022b)	Xiao et al. (2020)	Xiao et al. (2020)	Xiao et al. (2023a)	Cui and Qiang (2019)	Wu et al. (2020)	Jia et al. (2022a)	Jia et al. (2022b)	Xiao et al., 2023b	Beghetto et al. (2019a)	Gatto et al., 2021	

IUP 6, 2000 (ISO 3376, 2020): Physical and mechanical tests — Determination of tensile strength and percentage extension. IUP 8, 2000 (3377-2, 2016): Physical and mechanical tests — Determination of tear load — Part 2: Double edge tear. a) Chinese standard requirements: QB/T 1873–2010, William JLST 2000; b) IUP 40 Single edge tear (ISO 3377-1, 2002); c) IUP 12 (ISO 3378, 2002). Please note: The characteristics given in the table may be compared with the requirements for chromed leather, but under no circumstances can they be compared with each other.

after 8 h, hides were shaved and pickled to pH 3.5 and tanned for a second time with 10–30 wt% of tannin extracts by weight of shaved hides. This method allowed to reduce the quantity of tannins employed by about 75% compared to conventional vegetable tanning and significantly increase Ts of tanned leather as compared to SACC or vegetable tannins extracts alone. Pickling was necessary for the vegetable tanning phase, yet lower quantities of acids and NaCl where used compared to conventional vegetable tanning (Table 1). Moreover, SACC used in combination with Wattle or Bayberry gave very high Ts (91.7 °C). Further studies were devoted to verifying uptake efficiency of these combination tanning systems since higher uptake implies lower concentration of chemicals in the spent tanning bath and consequently lower environmental impact of wastewater. Generally, due to their higher reactivity, SACC in combination with condensed tannins showed higher uptake efficiency compared to hydrolysable tannins (respectively 85–90% and <85%).

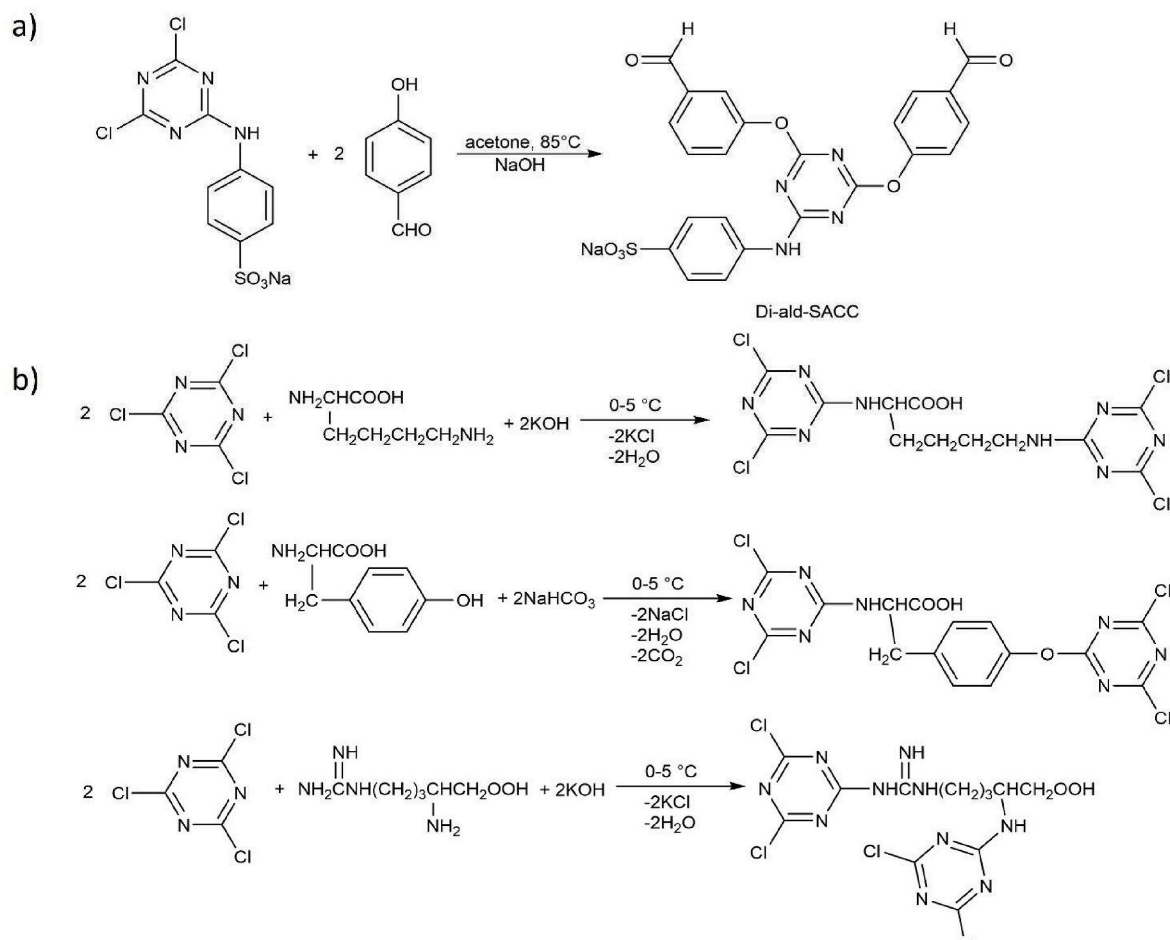
Another possible modification of SACC has been studied by Cui et al. (Cui and Qiang, 2019). Starting from SACC, the two chlorine atoms of the triazine are reacted with *p*-hydroxybenzaldehyde to give the corresponding dialdehyde (sodium 4-((4,6-bis(4-formylphenoxy)-1,3,5-triazin-2-yl)amino)benzenesulfonate (Scheme 2a) (Cui and Qiang, 2019).

Properties of tanned leather and commercial feasibility at pilot scale have been investigated and compared to a conventional CTP. As reported in Fig. 3c, the aldehydic groups present on Di-ald-SACC generate strong crosslinking covalent bonds with the amino groups of lysine or histidine, improving the hydrothermal stability and mechanical strength of the tanned leather, while the sulfonate ions contribute both to tanning effect and to improve the solubility of Di-ald-SACC in water. Adversely to SACC, when Di-ald-SACC was employed, pickling to pH 4.5–5.0 in the presence of 6–8 wt% sodium chloride was necessary since no chlorine atoms are present on the triazine and no HCl is formed during tanning, allowing for pickle-less processes. Ts of tanned leather prepared in the presence of 4 wt% of Di-ald-SACC reached 79 °C ± 4 °C, comparable to SACC but considerably lower to those achieved with SACC/Wattle combination system (Cui and Qiang, 2019; Kopitar et al., 2022; Xiao et al., 2023a).

6.2. 2,4,6-Trichloro-1,3-5-triazine derived tanning agents

An appealing innovative eco-friendly tanning process has recently been reported by Wu et al. based on TCT derived compounds containing natural amino acids (Wu et al., 2020) (Fig. 2 II, Scheme 2b). As for other triazine tanning agents, also in this case no pickling was required prior to the tanning process, with evident environmental benefits (see below). The synthesis and efficacy of three different TCT-amino acids, obtained by reaction of L-Lysine (L-Lys), L-Tyrosine (L-Tyr) or L-Arginine (L-Arg) and TCT was reported (Scheme 2b). When optimal wt% of L-Lys, L-Tyr, L-Arg TCT was used (20 wt% by weight of processed hide), Ts of sheep hides reached 82.5 °C, 81.2 °C and 80.3 °C respectively. Interestingly, the increase from two to four reactive chlorine atoms on the 1,3,5-triazine moiety does not seem to have a beneficial effect, since Ts obtained are lower than those obtained with SACC combination systems (86.5 °C SACC/TA and 91.7 °C SACC/Wattle), and also crust leather is stiffer (see Table 1).

Jia et al., in two different papers in 2022, reported the synthesis of polyethylene glycol triazines (PT) and a multi-site polyether amine



Scheme 2. Synthetic strategy for the production of a) sodium 4-((4,6-bis(4-formylphenoxy)-1,3,5-triazin-2-yl)amino)benzenesulfonate (Di-ald-SACC) and b) L-Lys-TCT, L-Tyr-TCT and L-Arg-TCT.

triazine (ET) (Scheme 3) and their use as pickle-free tanning agents (Jia et al., 2022a; Jia et al., 2022b).

PT were synthesized by reaction of TCT and dehydrated polyethylene glycol (PEG) of variable molecular weight (between 200 and 1000) in the presence of sodium carbonate. According to the authors, the molecular weight of PT tanning agents has a significant impact on the tanning effect, and in fact highest Ts (80.8 °C) were achieved with 24 wt % PT 800 by weight of processed hide. Moderately lower Ts were measured for PT600 and PT1000 tanned leather (about 79 °C), while PT200 and PT400 were unsatisfactory (Ts $\leq$ 77 °C).

Also in this case, the tanning of collagen with PT is attributed to the formation of covalent crosslinking bonds due to the reaction of PT active chlorine atoms with the pendant amino groups present in the collagen side chains (Yang et al., 2013).

ET were synthesized by the reaction of polyether amine (ED) with an excess of TCT to obtain four reactive linking sites (Scheme 3b).

These triazine derivatives have a similar reaction mechanism to PT and other 1,3,5-triazine tanning agents reported above. As for PT, also with ET, hides were treated at pH around 6, while similar Ts (79 °C) were achieved with halve the amount of ET (16 wt%) compared to 24 wt % by weight of leather processed with PT. Nevertheless, as for PT, the high number of active chlorine atoms present in ET does not appear particularly advantageous, since high tanning loads are used with no significant improvement in the characteristics of crust leather and environmental performances (Tables 1 and 2).

Based on the studies carried out on SACC/TA combination system, Xiao et al. (Xiao et al., 2023b) recently reported the synthesis of triazine-conjugated polyphenol derivatives obtained by reaction of tannic acid (TA), gallic acid (GA), and ellagic acid (EA) with TCT, aiming to reinforce polyphenol's crosslinking ability, and improve the filling capacity of triazine derivatives. The synthesis of TACC, GACC and EACC was carried out in very mild conditions, at pH between 8 and 6 allowing to minimize hydrolysis of TCT in water (Yan et al., 2008).

Alike other 1,3,5-triazine tanning agents reviewed in this paper, these triazine-conjugated polyphenols, lead to the formation of both covalent bonds and non-covalent interactions with skin collagen (Fig. 3d). According to ESI-MS analysis, molecular weight of TACC, GACC and EACC were consistent with structures bearing one or two TCT rings. According to the authors, best tanning efficiency may be achieved with compounds having molecular weight between 500 and 3000 Da.

As for others 1,3,5-triazines with a high number of active chlorine atoms, hydrothermal stability is lower (77 °C) compared to other SACC combination tanning agents reported by Xiao and coworkers , nevertheless physical mechanical properties of crust leather are good (Table 1), with half the dosage of tanning agent compared to traditional vegetable tanning methods (in best conditions 10 wt% GACC). Moreover, improvement in tannin exhaustion provides lower chemical load in wastewater generated (see Table 2) (Xiao et al., 2023 b).

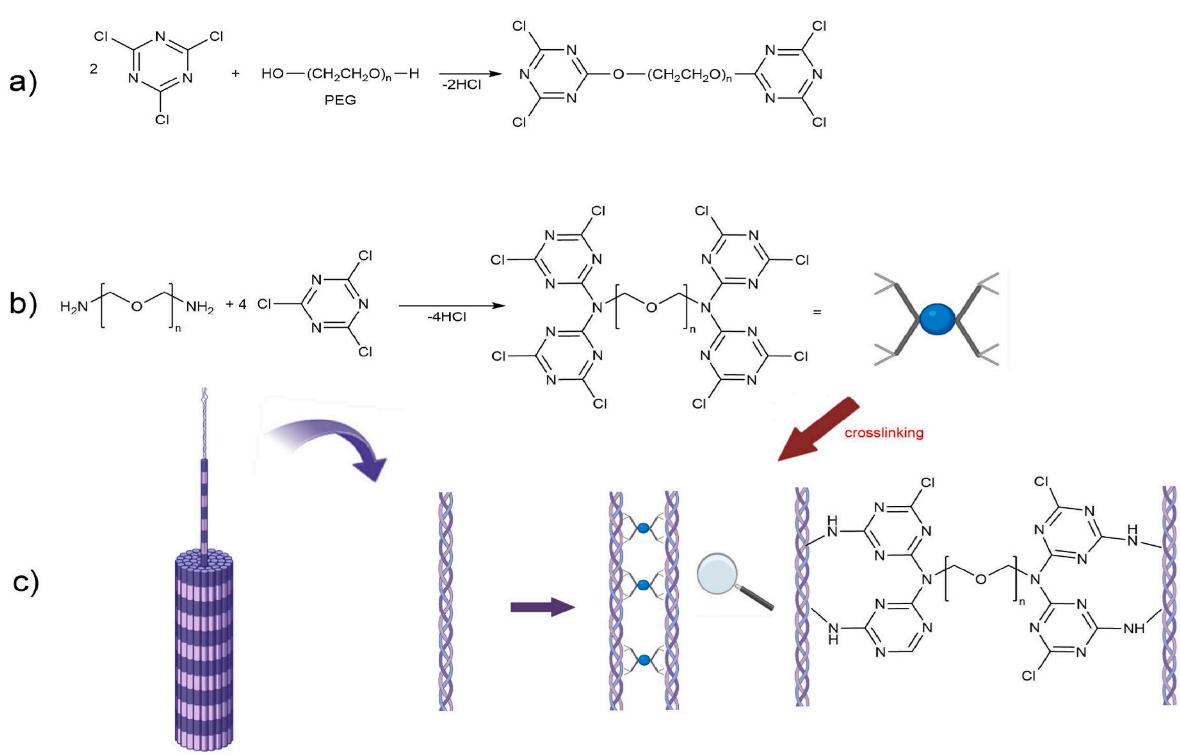
Additionally, Yu et al. reported the grafting of TCT on a conventional synthetic tannin prepared starting from *p*-hydroxy-sulphonic acid, urea, and formaldehyde, achieving a chlorine active condensation polymer (SACG), efficient as tanning agent (Ts 81.6 °C) (Yu et al., 2020b).

Considering recent restrictions on the use of formaldehyde (toxic, carcinogenic) and *p*-hydroxysulfonic acid which "causes severe skin burns and eye damage, may damage fertility and the unborn child, causes serious eye damage, is harmful if swallowed, may be corrosive to metals and may cause respiratory irritation" the use of syntans produced from formaldehyde and *p*-hydroxysulfonic acid are rapidly losing interest within the industry (https://echa.europa.eu). For this reason, this tanning system will not be further discussed.

For the sake of completeness, it may be mentioned that some combination tanning systems of SACC with metal salts have been reported by Cui et al. (Chromium salts) and Chen et al. (Titanium salts) (Chen et al., 2015; Cui et al., 2017).

6.3. 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride (DMTMM) and 2-chloro-4,6-dialkoxy-1,3,5-triazine derivatives

4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride (DMTMM) is a quaternary ammonium salt with excellent activity in promoting condensation and crosslinking reactions between carboxylic and aminic groups to produce amides (Beghetto et al., 2019b; D'Este



Scheme 3. Synthetic strategy for the production of a) PT, b) ET and c) crosslinking mechanism.

Table 2
Characteristics of tanning wastewater.

Tanning Agent	wt/wt (%)[a]	pH[b]	COD (g/L)	BOD_5 (g/L)	BOD_5/COD	TS (g/L)	TDS (g/L)	TSS (g/L)	TDC (g/L)	Cr(III) (g/L)	ER (%)
BCS[c]	5–10	4.2	2.0–5.0	0.6–0.9	0.18	30.0–60.0	29.0–58.0	1.0–2.5	15.0–25.0	1.5–4.0	72–80
SACC/Wattle[d]	10–15	3.0	13.2	4.6	0.35		8.5		3.2	0	92
GACC[e]	10	8.0	<5.0	0.8	<0.35				<7.5	0	90
Di-ald-SACC[f]	4	5.0	1.2–3.0	0.3–0.6	0.20–0.25	20.0–40.0	12.0–20.5	0.4–1.0		0	
L-Lys-TCT[g]	20	6.0-7-0	0.7–1.2	0.3–0.7	0.58	21.0–35.0	23.2–40.3	0.5–1.5		0	
PT[h,i]	16	6.0	1.3				40.7		9.6	0	79
ET[h,j]	8	6.0	1.2				38.0		8,8	0	80
DMTMM[c]	5–10	5.0	5.0–8.0	3.2–4.6	0.58–0.64	25.0–35.0	22.2–34.5	0.8–1.2	5.5–6.0	0	

COD: chemical oxygen demand; BOD_5: Biological oxygen demand at 5 days; TS. Total solid content; TDS: Total Dissolved Solids; TSS: Total suspended solids; TDC: Total dissolved chlorines; ER: Exhaustion rate.

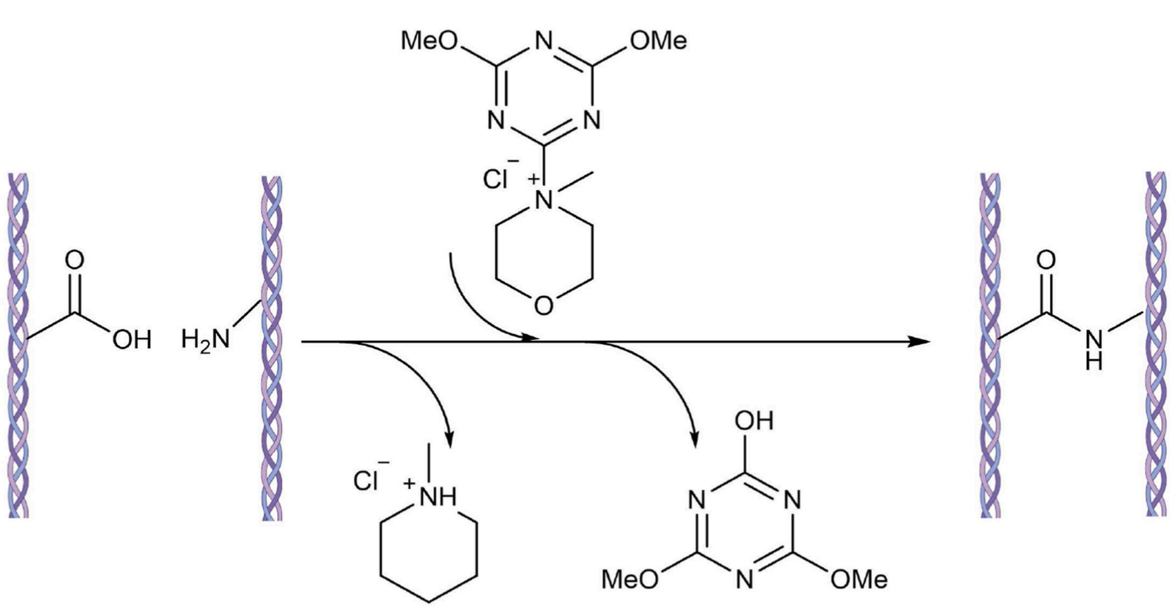
[a] Tanning agent wt% by wt of hide processed.
[b] pH at the end of the tanning process.
[c] Beghetto et al. (2019a); Chakraborty et al. (2008); Valeika et al. (2010); Xiao et al. (2023a); Zhu et al. (2020).
[d] Xiao et al. (2023a).
[e] Xiao et al., 2023b.
[f] Cui and Qiang (2019).
[g] Wu et al. (2020).
[h] Standard procedure according to AWWA, 1998.
[i] Jia et al. (2022a).
[j] Jia et al. (2022b).

et al., 2014; Falchi et al., 2000; Kaminski, 2000; Kitamura et al., 2020; Kunishima et al., 2002; Petta et al., 2016; Scrivanti et al., 2018), peptides (Al-Wahri et al., 2012; Beghetto et al., 2015; Damink et al., 1996, Duan and Sheardown, 2005; El Faham and Albericio, 2011; Montalbetti and Falque, 2005; Tiong et al., 2008; Kaminski, 2000; Kunishima et al., 1999, Kunishima et al., 2001, Scrivanti et al., 2019) and a variety of different materials (Beghetto et al., 2020; Sole et al., 2022). DMTMM is commonly referred to as "zero-length" crosslinking agent since it promotes the formation of covalent bonds, but it is not retained within the final product (Beghetto et al., 2019a; Cammarata et al., 2018; Kunishima et al., 1999). The use of DMTMM for leather tanning was first investigated and patented by Beghetto et al., in 2015 (Beghetto, 2015; Beghetto et al., 2019a). The commonly accepted reaction mechanism is depicted in Scheme 4 (Beghetto et al., 2019a; Kunishima et al., 1999); the key step is the addition of a carboxylic acid to the 1,3,5-triazine moiety to give an "active ester" intermediate which, in the presence of an amine, gives the corresponding amide. During the reaction DMTMM degrades forming non-toxic 2,4-dimethoxy-6-hydroxy-1,3,5-triazine (DMTOH) and 4-methylmorpholin-4-ium chloride (NMM-HCl) as byproducts.

Interestingly, when DMTMM is employed for leather processing, adversely to all tanning agents used by the industry, skin collagen is crosslinked without entrapment of the tanning agent, achieving high Ts (82–87 °C) with 4–5 wt% DMTMM by weight of processed hide. Good organoleptic and physical-mechanical characteristic together with low environmental impact were also reported (see Table 2).

As for other 1,3,5-tanning agents reported above (see Scheme 3) also DMTMM generates an acidic by product (DMTOH), which gradually reduces the pH of the tanning bath from 7 to 4.5–5.0, allowing to carry out an environmentally benign pickle-less process. Distinctively, the chlorine atom present on the triazine condensation agent does not release HCl but reacts with the *tert*-amine forming a non-toxic quaternary ammonium salt (NMM-HCl). This is an additional advantage reducing corrosion phenomena and also negative effects on collagen due to the lyotropic effect generated by HCl (Covington, 2009).

Starting from DMTMM which was the first tanning agent tested, a variety of different tanning agents were developed employing 4-(4,6-diethoxy-1,3,5-triazin-2-yl)-4-alkylammonium chlorides (DET-Ams) or 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) and 2-chloro-4,6-



Scheme 4. Proposed collagen crosslinking reaction mechanism in the presence of DMTMM.

diethoxy-1,3,5-triazine (CDET) in the presence of a *tert*-amine (CDMT/*tert*-amine or CDET/*tert*-amine, Fig. 2) (Gatto et al., 2021; Beghetto and Agostinis, 2017; Sole et al., 2021). Although the characteristics of the finished leather prepared with this class of 1,3,5-triazines are very similar, CDMT/*tert*-amine and CDET/*tert*-amine are easier to produce, cheaper and more versatile compared to DMTMM (Gatto et al., 2021). Ts of leather tanned with DMTMM, CDMT/*tert*-amine and CDET/*tert*-amine are between 82 and 90 °C, which is considerably higher than most of 1,3,5-triazines reported above.

Finally, it is worth mentioning that very recently Hao et al. reported the use of an innovative tanning agent starting from hexahydro-1,3,5-tris(hydroxyethyl)-*s*-triazine, ethylene glycol glycidyl ether and collagen peptide. This highly efficient system, nevertheless, is a non-aromatic 1,3,5-triazacyclohexane derivative, chemically different from other 1,3,5-triazines object of this review and, therefore, not be further discussed (Hao et al., 2023).

7. Physical mechanical characteristics of 1,3,5-triazine tanned leather

Different tanning processing conditions, comprehensive of pickling, if necessary, for conventional basic chromium sulphate (BCS) and different 1,3,5-triazine derivatives reviewed in this work are reported in Table S1 (see supplementary data). Main differences rely on the amount of water used, pickling, load of tanning agent, temperature, and time with variable impacts on the environmental sustainability of the different tanning processes (see below). In general, 1,3,5-triazine tanning agents do not require pickling and the tanning can be carried out immediately after conventional deliming-bating, therefore, chemicals consumption and wastewater impact is reduced. A summary of different Ts, together with different physical mechanical characteristics of tanned or crust leather prepared with CTP and different 1,3,5-triazine derivatives, is reported in Table 1.

From this comparison it emerges that most 1,3,5-triazine tanning agents reviewed in this work impart higher hydrothermal stability than vegetable and synthetic tannins (75–80 °C), and combination with other tannins is not mandatory. For example, L-Lys-TCT, ET, DMTMM and CDET/NMM give Ts values above 82.5 °C which is more than sufficient to process tanned hides into crust leather. It is nevertheless true that combination of SACC and tannins reported by Xiao et al., gave highest Ts (91.7 °C), comparable to CTP (Jia et al., 2022b; Xiao et al., 2023a).

Overall data reported in Table 1 are highly consistent, and physical mechanical properties, such as tensile and tear strength and elongation at break obtained using different 1,3,5-triazine tanning agents are generally comparable and similar to those obtained for chrome crust, complying with the standard requirements of the United Nations Industrial Development Organization (UNIDO) for upholstery leather (Di et al., 2006; Oaishi et al., 2023; Ork et al., 2014; Saravanabhavan et al., 2003; UNIDO, 2013). Tensile strength, which gives indications on the deformation performances of tanned hides, measured on L-Lys-TCT (16.2 N/mm^2), PT (15.3 $\pm$ 0.1 N/mm^2), ET (16.2 N/mm^2), DMTMM (21.0 $\pm$ 0.5 N/mm^2) and CDET/NMM (20.0 $\pm$ 0.5 N/mm^2) leather are very similar to chrome tanned leather (18.3 $\pm$ 0.1 N/mm^2). Analogous considerations apply for tear strength and elongation at break, except for tensile strength and elongation at break of Di-ald-SACC (Cui and Qiang, 2019), and tearing load of combination tanning SACC/Wattle which were measured according to different IUP standard tests (Xiao et al., 2023a). As regards organoleptic properties, such as softness, fineness, and fullness together with general appearance, are good and comparable to chrome tanned leather (Table 1). A significant difference between chrome and 1,3,5-triazine tanned hides is the colour, since BCS gives a characteristic blue colour, while 1,3,5-triazine tanned leather is generally white and therefore easier to dye.

8. Environmental impact of 1,3,5-triazine tanning technologies

Data collected to estimate the environmental impact of 1,3,5-triazine tannins have been compared with those of CTP (Beghetto et al., 2019a; Chakraborty et al., 2008; Valeika et al., 2010; Xiao et al., 2023a; Zhu et al., 2020) (Table 2).

As mentioned above, CTP requires pickling; this acidification step consumes about 80 kg of NaCl and 23–24 kg of weak and strong acids (sodium formiate and sulfuric acid) for ton of processed hides. Then, 8 kg of mild alkali salts are required to raise pH from 2.5 to 3.8 and promote the fixation of the metal within the hide. When triazines are used in combination with a vegetable tannin (SACC/TA, SACC/Wattle) or with amino acids (Lys-TCT), pickling is necessary, also in this case chemical consumption (acids, salt, and base) is lower compared to CTP or conventional vegetable tanning.

According to data reported in Table 2, chemical oxygen demand (COD), biological oxygen demand at five days (BOD_5), TS, TDS and TSS of wastewater produced with 1,3,5-triazine derivatives are lower compared to CTP. This innovative class of tanning compounds avoids or reduces sodium chloride consumption and consequently total dissolved chlorines present in wastewater (TDC) by 60–100 %, decreases the TS value by 40–60 %, TDS by 30–40 % and TSS by 40–60 % compared to chrome tanning. Only exception is the combination system SACC/Wattle for which COD and BOD_5 are higher than those of BCS (respectively 13.2 g/L and 4.6 g/L for SACC/Wattle, 2.0–5.0 g/L and 0.6–0.9 g/L for BCS), probably a consequence of the high amount of SACC and Wattle employed (15 wt%). Biodegradability of wastewater, measured as the ratio between BOD_5 and COD (Table 2), once more confirms the lower impact of 1,3,5-triazine tanning systems since for CTP BOD_5/COD is $<$ 0.25 (difficult to biodegrade), while in the presence of 1,3,5-triazines, BOD_5/COD is prevalently $>$0.45 (easier to biodegrade) (Ramesh et al., 2022).

Only Di-ald-SACC has a BOD_5/COD lower than 0.25, confirming that the presence of the aldehydic groups and the absence of free chlorine atoms, significantly reduces the environmental sustainability of Di-ald-SACC as tanning agents. Moreover, it is to point out that using 1,3,5-triazines no chromium is present in wastewater.

Exhaustion rate, which refers to the mount of tanning agent up taken by the leather, has also been reported in Table 2. From these data it emerges that SACC/wattle and GACC have an exhaustion rate approximately 20 % higher than BCS. Lower ER were observed with PT and ET, showing that also with 1,3,5-triazine derivatives the presence of vegetable tannins improves the exhaustion of the tanning agent. It is important to consider that also Cr(III) high exhaustion systems have been widely reported in the literature (Nashy and Eid, 2019; Zhu et al., 2020), and ER can be improved up to 94 %. It is important to underline that also with high exhaustion Cr(III) tanning systems the concentration of Cr(III) in wastewater is still very high (around 1.5 g/L), since according to the Italian waste directive the amount of residual Cr(III) after wastewater treatment should be 2 mg/L. Thus costly purification processes of wastewater are required to be within law limits (Dlgs, 152/2006).

9. Economic viability

Commercial viability and cost effectiveness are key factors in determining the success of a new product or process. Reduction in chemicals and water consumption, together with improved wastewater quality, constitute crucial environmental and socioeconomic advantages (https://www.life-imtan.eu/it/; https://www.codyeco.com/biopol/). To evaluate costs and savings of 1,3,5-triazine tanning agents necessary to process 1 ton of hides, data available in the literature for SACC, SACC/TA and SACC/Wattle combination systems, Di-ald-SACC, and DMTMM have been compared to BCS (Table 3).

Compared to BCS, pickle-less processes (SACC and DMTMM), completely avoid the use of NaCl, acids and bases, reducing chemicals

Table 3
Estimated costs and savings with BCS and 1,3,5-triazine tanning processes for 1 ton of hides processed.

	€/kg	BCS[a]			SACC[b]			SACC/TA[b]			SACC/Wattle[b]			Di-ald-SACC[c]			DMTMM[d]		
		(4% wt/wt)			(4% wt/wt)			(4%/10% wt/wt)			(10%/20% wt/wt)			(4% wt/wt)			(4% wt/wt)		
		%	kg	€	%	kg	€	%	kg	€	%	kg	€	%	kg	€	%	kg	€
NaCl	0.11	8	80	8,8										4	40	4.4			
H_2SO_4	0.15	1	11	1,7										1	5	0.8			
HCOOH	1.30	1	12	15.6				1	5	6.5	0.5	5	6.5	0.4	4	5.2			
BCS	1.20	4	40	48															
SACC	2.70				4	40	108	4	40	108									
TA	7.40							10	100	740	10	100	270						
Wattle[e]	3.00										20	62.5	187.5						
Di-ald-SACC	2.30													4	40	92			
DMTMM	4.50																4	40	180
Base	0.32	1	8	2.6				1.5	15	4.8				2	20	6.4			
Water	0.03	200	2000	60	100	1000	30	210	2100	63	320	3200	96	100	1000	30	100	1000	30
WWT[f]	0.12	200	2000	240	100	1000	120	210	2100	252	320	3200	384	100	1000	120	100	1000	120
Total €			**376.61**			**258.00**			**1174.30**			**948.80**			**258.75**			**330.00**	
Savings €[g]						**−118.61**			**+ 797.69**			**+ 572.19**			**−117.86**			**−46.61**	

[a] Beghetto et al. (2019a), Wu et al. (2020).
[b] Xiao et al. (2023a).
[c] Cui and Qiang (2019).
[d] Beghetto et al. (2019b).
[e] wt% Wattle calculated on the weight of shaved hides after SACC tanning (250 kg).
[f] WWT: Wastewater treatment cost.
[g] Difference in costs between BCS and 1,3,5-triazine tanning.

consumption by over 110 kg for 1000 kg of processed hides, with a saving of about 29.0 €. When 1,3,5-triazines are used in combination with vegetable tannins (SACC/TA and SACC/Wattle, Table S1), moderate pickling is required to promote their penetration inside the hides. Additionally, significant quantities of TA or Wattle are employed so that overall chemical consumption and costs are higher, respectively 160 kg (859.30 €) for SACC/TA and 170 kg (468.80 €) for SACC/Wattle, compared to BCS (151.0 kg, 76.70 €). When Di-ald-SACC is used, chemical consumption is lower compared to BCS (−42.0 kg) but at a higher price (108.80 €); additionally, pickling is required and biodegradability of wastewater is very similar to that of CTP (BOD_5/COD 0.20 and 0.18 respectively, see Table 2). Thus, as previously discussed the absence of active chlorine atoms on the (1,3,5-triazin-2-yl)amino)benzene sulphonate moiety (Fig. 2), together with the presence of aldehydic functionalities, makes Di-ald-SACC very different from other 1,3,5-triazines reviewed in this paper.

Considering processing costs, although SACC and DMTMM cost up to four times the price of BCS (2.70 €/kg SACC and 4.50 €/kg DMTMM compared to 1.20 €/kg for BCS), savings are achieved due to the reduction in water consumption and wastewater treatment costs. In fact, the most competitive advantage of SACC and DMTMM tanning is not only due to direct water savings but to reduced costs in wastewater treatment (-120 € compared to BCS, see Table 3).

Data reported in Table 3 clearly show that when the whole process is considered, with an approach from cradle to grave, different impacts and costs emerge so that even tanning agents four times more expensive than BCS, may become cost effective. It should be further stressed that savings reported in Table 3 could further be improved considering the lower cost for triazine wastewater treatment compared to that of BCS. Moreover, the use of SACC and DMTMM do not require changes in the protocols or machinery presently employed by the leather industry. On the contrary, they simplify the process avoiding pickling and basification with the economic and environmental benefits illustrated above.

10. Conclusions

As the industry continues to evolve, there is a growing emphasis on sustainability, transparency, and innovation. Both in luxury and mass sectors, the demand for sustainable and traceable leather products is growing, driving the adoption of certifications like those of the Leather Working Group (LWG, https://www.leatherworkinggroup.com/) and the Institute of Quality Certification for the Leather Sector (I.CE.C, https://www.icec.it/en/certificazioni/sostenibilita-aziendale/certification-of-companies-sustainability). Balancing environmental concerns, ethical practices, and market demands presents both challenges and opportunities for stakeholders in the leather industry.

Due to the new regulations and the increasing awareness of consumers on pollution mitigation, the leather industry is transitioning to a new environmentally sustainable phase. In synergy with the scientific community, there is a common effort to find eco-friendly solutions to reduce the influence of tanning processes on the environment. As indicated by the last Best Available Techniques reference document on the tanning of hides and skins (Best Available Techniques, 2013), several indicators have been recognized, significantly reducing the environmental impact of leather processing.

Within this panorama the use of 1,3,5-triazine derivatives as tanning agents appears as a sound, economically, and environmentally sustainable solution for the production of chrome, phenol, and aldehyde-free leather. According to a recent review by Hassan (Hassan et al., 2023) on alternatives to chrome tanning, it appears that many solutions have been developed over the years, none of which are considered to provide equivalent tanning efficiency, organoleptic and physical mechanical characteristics, comparable to chrome tanning. Nevertheless, this extensive review did not take into consideration any of the 1,3,5-triazines here reported which, on the contrary, appear as a viable alternative to chrome tanning from all prospectives. As reported in this review it emerges that from 2019 to 2023 many papers and patents have been published on the use, environmental and economic efficacy of various 1,3,5-triazines such as SACC, vegetable tanning combination systems (SACC/TA, SACC/Wattle), Di-ald-SACC, PT, ET, GACC and DMTMM (Fig. 2), allowing to produce leather with comparable characteristics to BCS leather and reduced impact on the environment and human health. In particular, SACC and DMTMM are most appealing, due to pickle-less tanning and high reduction in chemicals and water consumption together with lower amounts of wastewater produced, having improved biodegradability. Furthermore, considering the overall impact of the tanning process, although SACC and DMTMM are more expensive than BCS, savings are generated due to the environmental benefits derived. Thus, based on the data analysis reported in this review, 1,3,5-triazines derivatives may play an important role in the green transition of the leather industry, to fulfil the goals of the ONU Agenda 2030.

CRediT authorship contribution statement

Manuela Facchin: Writing – review & editing, Supervision, Formal analysis, Data curation. **Vanessa Gatto:** Writing – review & editing, Data curation. **Riccardo Samiolo:** Formal analysis, Data curation. **Silvia Conca:** Writing – review & editing, Data curation. **Domenico Santandrea:** Writing – review & editing, Formal analysis. **Valentina Beghetto:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Valentina Beghetto reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.123472.

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