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Review

Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review

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HIGHLIGHTS

- Wastewater characteristics depend on the chemicals used in tannery processes.
- In plant control is the best option to minimize water consumption and chemicals use.
- Emerging treatment technologies are in advance as treatment of tannery wastewaters.

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ABSTRACT

Although the leather tanning industry is known to be one of the leading economic sectors in many countries, there has been an increasing environmental concern regarding the release of various recalcitrant pollutants in tannery wastewater. It has been shown that biological processes are presently known as the most environmental friendly but inefficient for removal of recalcitrant organics and micro-pollutants in tannery wastewater. Hence emerging technologies such as advanced oxidation processes and membrane processes have been attempted as integrative to biological treatment for this sense. This paper, as the-state-of-the-art, attempts to revise the over world trends of treatment technologies and advances for pollution prevention from tannery chemicals and wastewater. It can be elucidated that according to less extent advances in wastewater minimization as well as in leather production technology and chemicals substitution, biological and chemical treatment processes have been progressively studied. However, there has not been a full scale application yet of those emerging technologies using advanced oxidation although some of them proved good achievements to remove xenobiotics present in tannery wastewater. It can be noted that advanced oxidation technologies integrated with biological processes will remain in the agenda of the decision makers and water sector to apply the best prevention solution for the future tanneries.

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1. Introduction

Leather tanning is a wide common industry all over the world. It is known to be one of the most important industries in Mediterranean countries (Insel et al., 2009; Mannucci et al., 2010). Because of their complex wastewater characteristics leather tanneries are generally located in so called *organized industrial districts*. In Italy tanneries, represented by about 1400 tanneries, are sited in four main poles: Veneto, Toscana, Lombardia and Campania regions (Fig. 1a); they transform raw or wet-blue skins into products used for various purposes. The value of production weighs for 17% of worldwide production and for 62% considering only the European Union. In terms of trade, it has been calculated that nearly one out of three skins traded between international operators is of Italian origin (UNIC, 2013). A proportional distribution of the leather tanneries in Italy and in EU countries is shown in Fig. 1b.

Tanneries represent an important economic field also in developing countries as in the cases of Turkey, China, India, Pakistan Brazil and Ethiopia (Orhon et al., 1999; Leta et al., 2004; Lefebvre et al., 2006; Banu and Kaliappan, 2007).

Currently the aqueous streams of each exhausted bath of tanning process are mixed all together in balancing tanks and pre-treated before biological treatment (Cassano et al., 2001; Dogruel et al., 2006; Lofrano et al., 2006). However the mixture of many compounds used in the process can be released into the environment because they even remain after conventional treatment and negatively affect organisms (Kumar et al., 2008; Siqueira et al., 2011) and environment (Meriç et al., 2005; Oral et al., 2007; Shakir et al., 2012; Alvarez-Bernal et al., 2006; Tigini et al., 2011) or may inhibit nitrification process (Jochimsen and Jekel, 1997; Szpyrkowicz et al., 2001). The effluent of leather tanneries was associated to a huge foaming problem on surface waters too (Schilling et al., 2012).

The high concentrations of pollutants with low biodegradability in tannery wastewater represent a serious and actual technological and environmental challenge (Di Iaconi et al., 2002; Schrank et al., 2009). Much research has addressed this aim over the past decade highlighting the promising role of a special class of oxidation techniques defined as advanced oxidation processes (AOPs) to treat tannery wastewater and synthetic and natural tanning materials (Szpyrkowicz et al., 2001; Dantas et al., 2003; Dogruel et al., 2004; Schrank et al., 2005; Pokrywiecki Sauer et al., 2006; Kurt et al., 2007; Preethi et al., 2009; Di Iaconi et al., 2010; Lofrano et al., 2007a,b, 2010a,b). Thus, the leather industry is being pressured to search cleaner, economically as well as environmentally sustainable wastewater treatment technologies (Suresh et al., 2001; Sundarapandiyan et al., 2010; Krishnamoorthy et al., 2012).

This paper presents the state-of-the art of chemical minimization and treatment technologies applied to leather wastewater. An introduction of the common production technologies, water consumption and wastewater characteristics is first presented and accordingly wastewater treatment options are compared, taking into account several criteria. Additionally the greening production and advances in treatment technology is discussed.

2. Tannery industry

2.1. Leather production and chemicals used

The tanning process aims to transform skins in stable and imputrescible products namely leather (Fig. 2). There are four major groups of sub-processes required to make finished leather: beamhouse operation, tanyard processes, retanning and finishing (U.S. EPA, 1986; Tunay et al., 1995; Cooman et al., 2003). However for each end product, the tanning process is different and the kind and amount of waste produced may vary in a wide range (Tunay et al., 1995; Ates et al., 1997) (Fig. 3). Traditionally most of tannery industries process all kind of leathers, thus starting from dehairing to retanning processes. However in some cases only pre-pickled leather is processed with a retanning process. Table 1 shows a typical retanning bath procedure applied for production of clothing leathers in a large leather tannery district, Southern Italy. A similar procedure was reported by Saravanbahavan et al. (2004) and by Basaran et al. (2008) for Indian and Turkish leather tanneries respectively.

Acids, alkalis, chromium salts, tannins, solvents, sulphides, dyes, auxiliaries, and many others compounds which are used in the transformation of raw or semi-pickled skins into commercial goods, are not completely fixed by skins and remain in the effluent. For instance the present commercial chrome tanning method gives rise to only about 50–70% chromium uptake (Saravanbahavan et al., 2004). During retanning procedures, synthetic tannins (Syntan), oils and resins are added to form softer leather at varying doses (Lofrano et al., 2008). One of the refractory groups of chemicals in tannery effluents derives mainly from tannins (Di Iaconi et al., 2010). Syntans are characterized by complex chemical structures, because they are composed of an extended set of chemicals such as phenol-, naphthalene-, formaldehyde- and melamine-based syntans, and acrylic resins (De Nicola et al., 2007; Lofrano et al., 2007a; Munz et al., 2009). Among syntans, the ones based on sulfonated naphthalenes and their formaldehyde condensates play a primary role, for volumes and quantity used in leather tanning industry (Munz et al., 2009). According to Fig. 4, the oils cover the greater COD equivalents compared to the resins and syntans. The BOD_5/COD ratio of syntans was also lower than other compounds (Lofrano et al., 2007a). However it is worth to notice as no one of these

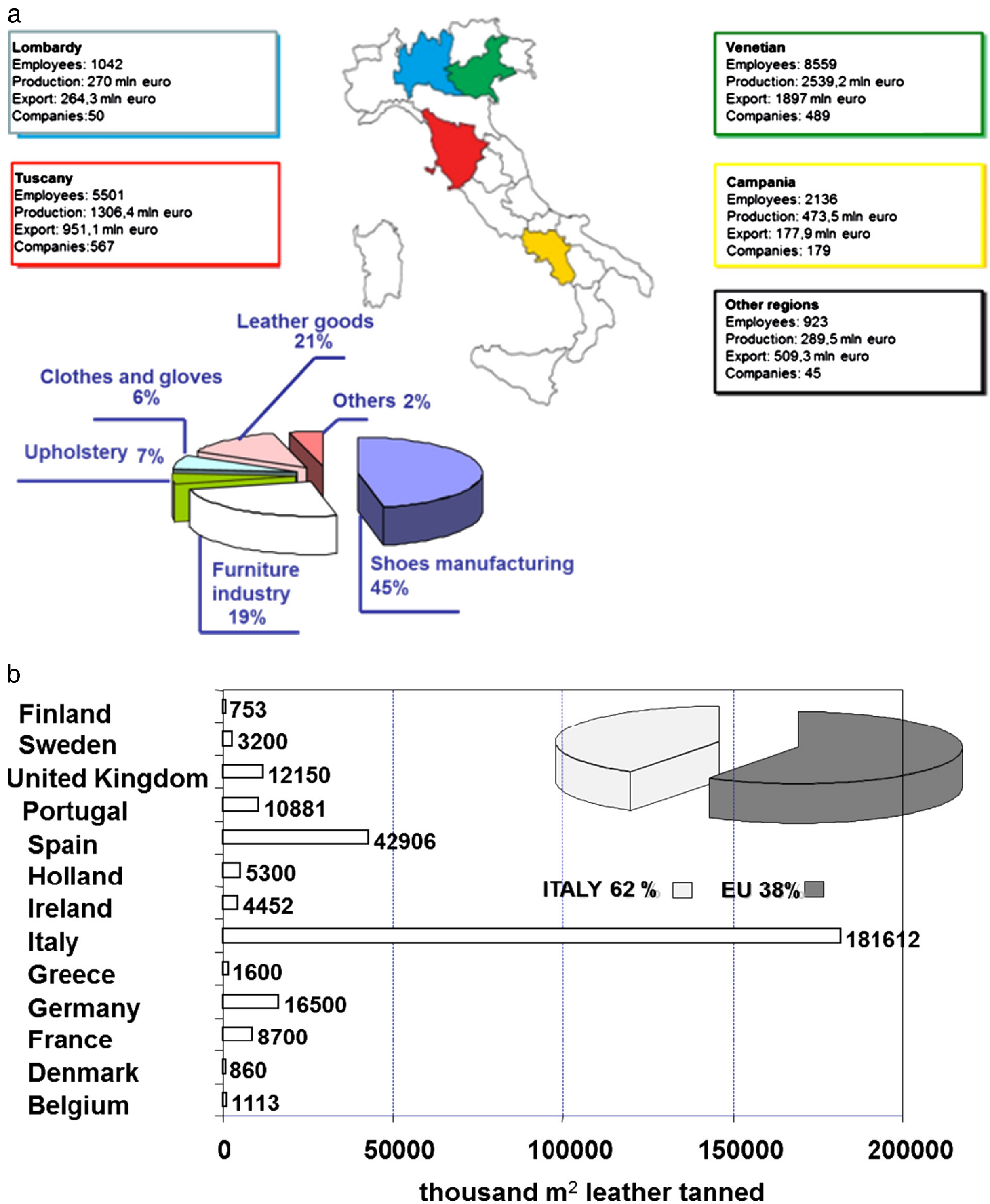

Fig. 1. Spatial distribution of leather tanneries in Italy (a) and among the member states (b) (elaboration from data UNIC, 2013).

compounds show a BOD_5/COD ratio higher than 0.4, indicating a very low biodegradability of each of them.

Among the various alternatives for chromium, vegetable tannins are considered to be ecofriendly because of its natural origin. However, this tanning leads to excessive loading in the leathers, which reduces its versatility to make different end products and also has low resource availability (Krishnamoorthy et al., 2012). Recently the toxicity of mimosa tannin and phenol-based syntan was tested for toxicity to sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) early development and to marine algal cell growth (*Dunaliella tertiolecta*) comparatively by De Nicola et al. (2007). They observed that the sea urchin embryogenesis was affected by vegetable tannin and syntan water extracts at levels of 1 mgL^{-1}. In contrast to the previous regulations such as Integrated Pollution Prevention and Control Directive ((96/61/EC, 1996; 2008/1/EC, 2008), the new European regulatory framework on chemicals namely Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH, (EC 1907/2006) which entered into force on 1 June 2007, places obligations not only on the

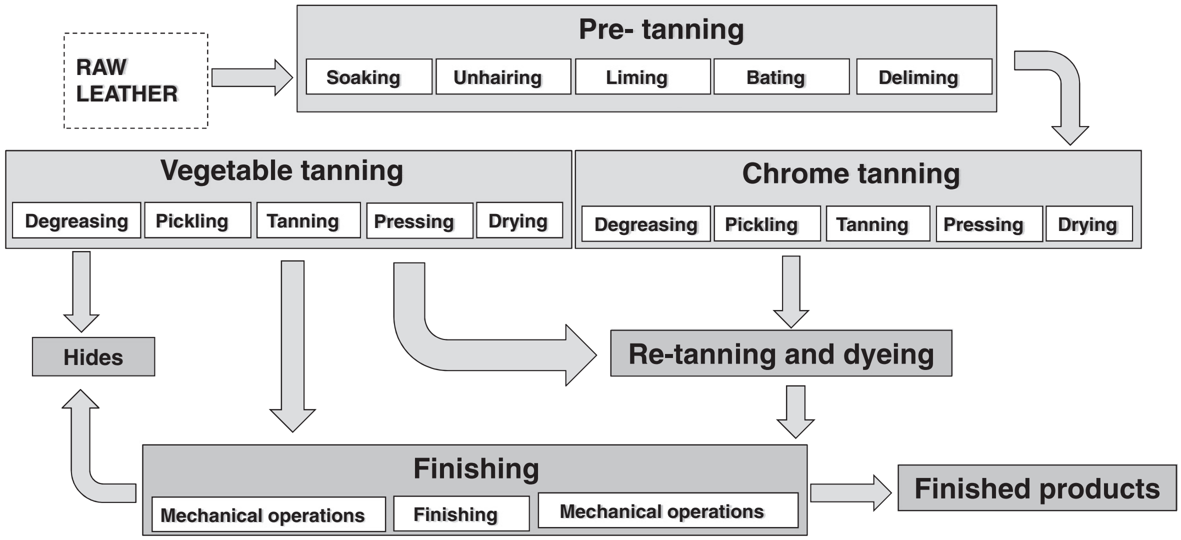

Fig. 2. A typical process flow sheet in an integrated leather tannery industry.

chemical manufacturer, but also on the industrial user of chemicals as well. Therefore tanneries have to fulfil user obligations under REACH. The tanneries must only use leather auxiliaries and basic chemicals for those uses which the registrant has considered in the registration dossier and which have therefore been listed in the Safety Data Sheet. Moreover, when the Directive 2003/53/EC entered into force, the marketing and use of products and product formulations that contain more than 0.1% of nonyl ethoxyphenol (NPE) or nonylphenol (NP) in Europe has been restricted for leather products too. However, there has not been any particular restriction for syntans yet.

2.2. Wastewater generation and characterization

An average of 30–35 m^3 of wastewater is produced per ton of raw hide. However, wastewater production varies in wide range (10–100 m^3 per ton hide) depending on the raw material, the finishing product and the production processes (Tunay et al., 1995). Organic pollutants (proteic and lipidic components) are originated from skins (it is calculated that the raw skin has 30% loss of organic material during the working cycle) or they are introduced during processes.

Table 2 summarizes the average composition of tannery processes effluents. The beamhouse wastewater is characterized by an alkaline pH and the tanning effluent by a very acidic pH as well as high COD. Tunay et al. (1995) reported COD value of (27,600 mgL^{-1}) for beamhouse wastewater. The highest amount of the salt load occurs in the beamhouse area. About 15% (w/w) to 40% (w/w) of common salt is used for preserving animal skins and it is removed during the soaking (Sundarapandiyan et al., 2010). Lime and sodium sulfide or sulfydrate are normally used during liming-unhairing operation. Organic solvents are most widely used chemicals in degreasing step producing a considerable increase of environmental pollution by emission of volatile compounds (Cassano et al., 2001). If a tannery is processing salted hides then the biggest salt component in the wastewater is always the sodium chloride from hide and skin preservation. The wet-end re-tanning, dyeing and fat liquoring processes have only a minor impact on the total salt load dominantly originated from the hides in the initial pre-soak and main soak (Fig. 3). The tanning wastewater contain the highest concentration of total chromium (up to 4950 mgL^{-1}) (Cooman et al., 2003). Coloring usually involves combining dyes with the tanned skin fibers to form an insoluble compound. Retanning and wet finishing streams are relatively low in BOD and TSS, high in COD and contain trivalent chromium, tannins, sulfonated oils and spent dyes (U.S. EPA, 1986).

Table 3 reports the average composition of mixed effluents of leather tanneries. The average influent chromium (III) concentration varies in a wide range (30–260 mgL^{-1}) depending on the tanning process applied. Very high salinity is reflected by a concentration of TDS (37,000 mgL^{-1}). Generally tannery effluents are rich in nitrogen, especially organic nitrogen but very poor in phosphorous. Although COD is the most common parameter used in tannery wastewater characterization, TOC is more reliable than COD since the high concentration of chlorides and sulphides of these effluents can affect significantly the analysis of COD.

2.3. Biodegradation characteristics

The BOD_5/COD or BOD_5/TOC ratios continue to be used for biodegradability information. However BOD is a controversial parameter when it is applied to tannery wastewater since it contains many inhibitors (Ates et al., 1997). Regarding the COD measurement, it can give more reliable information about the composition of this kind of wastewater. Tannery wastewater requires COD fractionation for the identification of biodegradable and inert COD components (Orhon et al., 1999). Results on COD fractionation of tannery influent by various researchers are summarized in Table 4. A high ratio of 52% of the total COD for the particulate inert fraction (X_{I1}) had been reported in the literature (Karahan et al., 2008). This was correlated with the inhibitor effect of the particulate portion of the tannery wastewater.

An inert soluble COD and particulate COD fractions corresponding to 9% and 13% of the total COD, respectively were reported in another study carried out from the settling tank of a centralized tannery wastewater treatment plant, located in Tuzla (Turkey) (Dogruel et al., 2006).

Integration of physical particle size distribution of COD with COD fractionation has been recently studied for a better interpretation of COD fractions and biodegradability. Karahan et al. (2008) applied this approach for tannery wastewater and reported that the 60 % of the influent COD was at the particulate fraction while 25% of the total COD was determined as soluble and 15% was at the colloidal fraction. The readily biodegradable fraction (S_{S1}) was entirely at the soluble range (<2 nm). The majority (83%) of the rapidly hydrolysable fraction (S_{H1}) was at the soluble range, and only a minor portion (17%) was at the colloidal range (13–220 nm). 11% of the soluble inert fraction (S_{I1}) was at the soluble range, whereas the rest (89%) was distributed over the colloidal range (2–1600 nm).

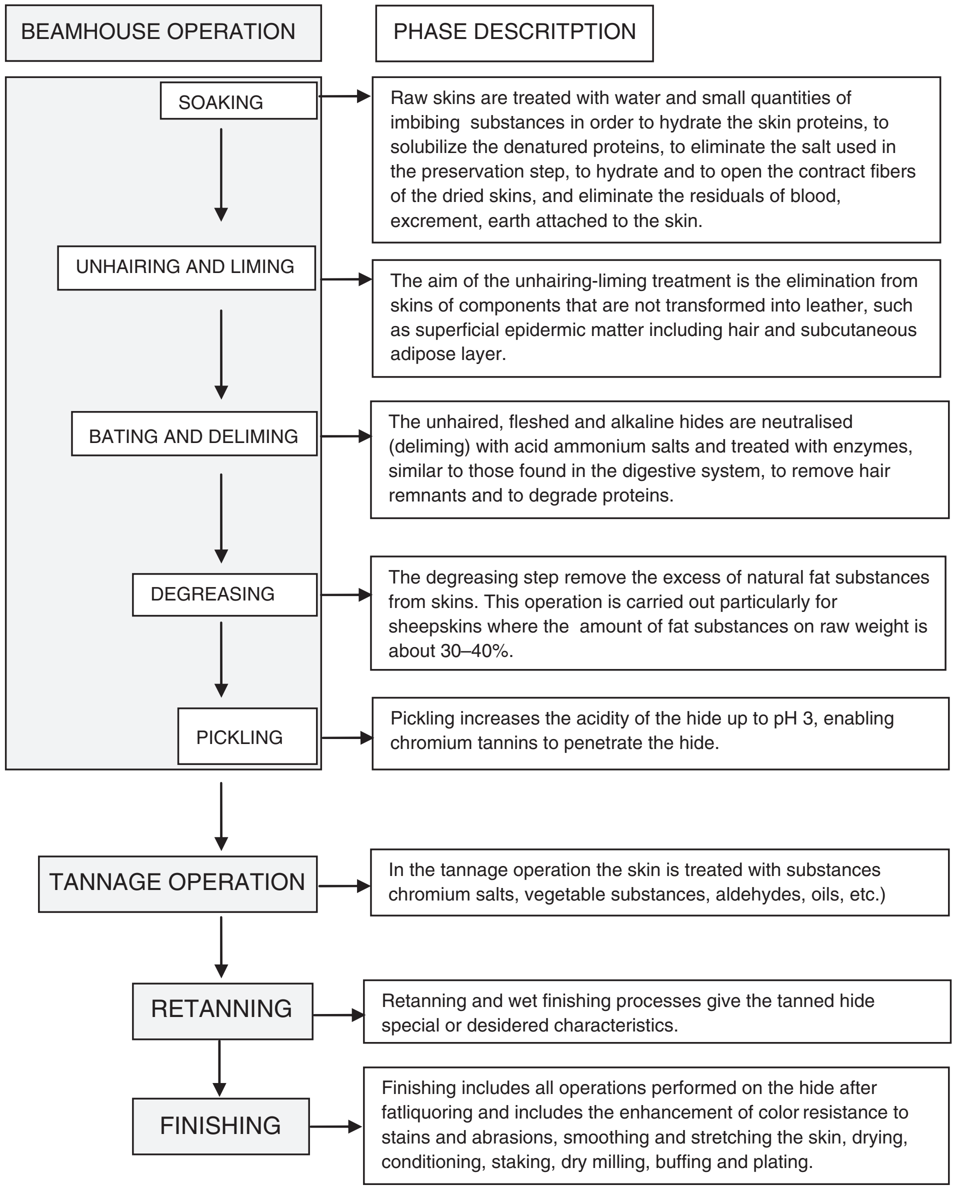

Fig. 3. Description of unit processes in leather production.

3. Treatment options

3.1. Coagulation and flocculation

The coagulation/flocculation (CF) of tannery wastewater process has been investigated using inorganic coagulants such as aluminium sulphate ($AlSO_4$), ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) to reduce organic load (COD) and suspended solids (SS) as well as to remove toxic substances, e.g. chromium before biological treatment (Ates et al., 1997; Kabdasli et al., 1999; Song et al., 2004; Lofrano et al., 2006).

Each coagulant operates most effectively in a specific pH. The extent of the pH range is affected by the type of coagulant used and by the characteristics of the wastewater as well as by the dosage of coagulant (Song et al., 2004). Ates et al. (1997) investigated the effectiveness of alum and $FeCl_3$ based-CF for the treatment of homogenized inlet of a central treatment plant of leather tanneries district, Turkey. All experiments resulted in >70% of COD removal. Total chromium was also effectively (<5 mgL^{-1}) removed by alum while it was almost completely removed using $FeCl_3$. Kabdasli et al. (1999) also reported 40–70% removal of COD and >99% of total chromium from leather tanning wastewater using $FeSO_4$, $FeCl_3$ and alum. Song et al. (2004) obtained a removal range of 30–37% of total COD, 74–99% of chromium and 38–46% of SS using 800 $mgL^{-1}$of alum at 7.5 pH for pre-settled tannery wastewater containing 260 mgL^{-1} of SS, 16.8 mgL^{-1} of chromium, 3300 $mgL^{-1}$of COD at pH 9.2. They reported that $FeCl_3$ proved better results than alum.

To improve the coagulation efficiency as well as to minimize residual coagulants in the effluent (Gao et al., 2004) new types of coagulants have been developed such as poly aluminium chloride (PAC), poly aluminium silicate (PASiC) and poly aluminium ferric chloride (PAFC) ($[Al_2(OH)_nCl_6\text{-}n]m$. $[Fe_2(OH)nCl_6\text{-}n]m$). Lofrano et al. (2006) carried out a series of jar tests experiments on raw wastewater samples taken from the effluent of the equalization basin of the wastewater treatment plant in a large tannery district in Southern Italy (COD 12,415–14,820 mgL^{-1}). More than 75% of COD removal was obtained at all doses of alum (800–900–1000–1200 mgL^{-1}) using PAFC. The optimum conditions were assessed as pH 8.5 and 900 mgL^{-1} of PAFC

Table 1
A retanning procedure applied in the leather tanning district to process 1–2 kg of Nappa leather production (Lofrano et al., 2008).

Operations	% for 100 g leather	Chemicals used	pH	Time [min]
Degreasing	150	H_2O 45 °C		
	1.0	Ethoxylated nonylphenol (NPE)	3.8	40′
	0.5	Ossalic acid		
Bolt down and washing	100	H_2O 40 °C		
Chrome retanning	1	Phosphoric Oil		30′
	0,15	Formic acid (85%)		10′
	2	Chrome (IV)		
	4	Synthetic chrome (R1)		
				12 h
Bolt down	200	H_2O 40 °C		
	2.0	Synthetic Salts		20′
	0.8	Sodium bicarbonate		20′
Neutralization	1	Amino plastic resin	5.5	30′
Bolt down and washing	150	H_2O 55 °C		
Re-tanning	2	Plastic Resins		30′
	4	Soya Lecithin		10′
	3	Sulfunated oil		
	1	Sulphonated oil		
	3	Vegetal oil		
			3.5	60′
	3	Syntan (ST2)		30′
	3	Dye		
	3	Amino plastic resin		30′
	3	Formic acid (85%)		40′

with the pH adjustment using $Ca(OH)_2$ which resulted in high removal of COD (>75%) and TSS (>95%) and reduced *Daphnia magna* immobilization (<50%).

3.2. Biological treatment

3.2.1. Aerobic processes

Biological processes are usually prescribed for treating industrial effluents to reduce organic content as they have economic advantages over chemical oxidation (Dogruel et al., 2006). However high concentration of tannins and other poorly biodegradable compounds as well as metals can inhibit biological treatment. Stasinakis et al. (2002) observed a significant inhibition of heterotrophic growth in the presence of 10 mgL^{-1} Cr(VI). Farabegoli et al. (2004) reported that chromium concentration had less influence on denitrification bacteria than on nitrification bacteria.

A typical Sequencing Batch Reactor (SBR) has been proven to be more capable of carrying out biological processes such as nitrification and denitrification in the presence of inhibiting substances (Farabegoli et al., 2004; Ganesh et al., 2006) due to the selection and enrichment of particular microbial species. The performance of SBR for nitrogen removal in tannery wastewater with a wide range of temperature (7 to 30 °C) was studied and full nitrification and denitrification was maintained by

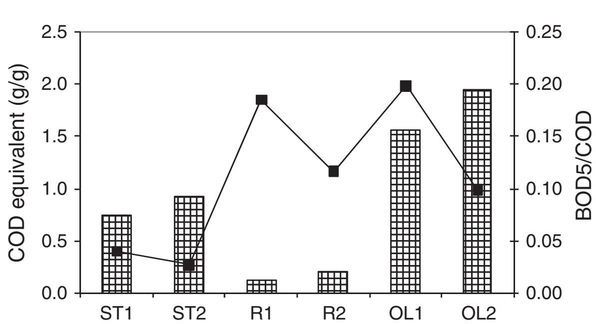

Fig. 4. Comparison of organic contents (COD equivalents *vs.* BOD_5/COD) of some re-tanning agents. Resin (R), syntan (ST), oils (OL).

adjustment of the sludge age for each temperature range (Murat et al., 2006). The authors described the SBR technology as a reliable treatment for tannery wastewater due to the flexibility of its operation.

The biodegradation of naphthalene-2-sulfonic acid which is a main component of the naphthalenesulfonate, by *Arthrobacter* sp. 2AC and *Comamonas* sp. 4BC was reported and these two bacterial strains were isolated from tannery activated sludge (Song et al., 2005). Song and Burns (2005) described the degradation of all components of the condensation product of 2-naphthalenesulfonic acid and formaldehyde (CNSF), by fungus *Cunninghamella polymorpha*. They suggested a combination of *C. polymorpha* and *Arthrobacter* sp. 2 AC or *Comamonas* sp. 4BC for the treatment of tannery wastewater. Conventional cultures could not treat saline wastewaters of values higher than 3–5% (w/v) and shifts in salt concentration causing significant failures in system performance. Senthilkumar et al. (2008) isolated *Pseudomonas aeruginosa*, *Bacillus flexus*, *Exiguobacterium homiense*, and *Staphylococcus aureus* from soak liquor, marine soil, salt lake saline liquor and seawater, respectively and studied the biodegradation of tannery soak liquor by these halotolerant bacterial consortia. An appreciable COD removal (80%) was observed at 8% (w/v) salinity for mixed salt tolerant consortia but increase in salt concentration to 10% (w/v) resulted in a decrease in COD removal efficiency.

The presence of sulphide, chromium, chloride and fluctuation in temperature has adverse effects on nitrification process. The impact of temperature on organic carbon and nitrogen removal had been studied for a full-scale industrial activated sludge plant treating leather tanning wastewaters (Görgün et al., 2007). It was observed that the temperature changes had a minor influence on COD removal efficiency (4–5%) while the total nitrogen removal was highly affected by the temperature. Insel et al. (2009) investigated the performance of intermittent aeration type of operation when temperature was fluctuated between 21 and 35 °C. The increase in the aeration intensity improved the nitrification performance and the application of intermittent aeration improved the total nitrogen removal to around 60%.

3.2.2. Anaerobic processes

There has recently been growing interest within the scientific community regarding the anaerobic treatment of tannery wastewater due to the several drawbacks of its application: i) the implementation of adequate technology for H_2S desorption and treatment is required due to the consistent production of sulfide as a result of the reduction of sulfate which occurs in the absence of alternative electron acceptors such as oxygen and nitrate; ii) high protein component affects selection of biomass, slow kinetics of hydrolysis, inhibits granular sludge formation.

Mannucci et al. (2010) reported 63 articles dealing with the application of anaerobic processes in tannery wastewater treatment in the period from 1979 to 2008. Among them, 12 referred to vegetable tannery wastewaters or to synthetic wastewater simulating vegetable tannery wastewater, while the remaining referred to chromium tannery wastewater.

The anaerobic treatment of tannery wastewaters are mainly performed by using anaerobic filters (AF) composed of both upflow anaerobic filters (UAF) and down-flow anaerobic filters (DAF) and Upflow Anaerobic Sludge Blanket (UASB) reactors (Lefebvre et al., 2006; El-Sheikh et al., 2011). Only a few experiments refer to expanded granular sludge bed (EGSB) and to anaerobic baffled reactor (ABR) (Zupančič and Jemec, 2010).

Polyurethane foam cubes and polypropylene rashing-rings are mainly used as filling materials of anaerobic filters (Daryapurkar et al., 2001). Besides, the control parameters include the specific organic load rate (OLR), the hydraulic retention time (HRT) which can varies in a wide range, from 12 h to 5 days, temperature, degree of mixing, composition of the wastewater (sulfate concentration) and the characteristics of growth and maintenance of microorganisms.

Table 2
Average composition of tannery effluents baths (adapted from Lofrano et al., 2010a,b).

Parameters	Soaking		Unhairing liming		Bating deliming		Pickling	Chrom. tanning	Re-tanning		References
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
pH	6	10	12.5	13	6	11	4	3.2	4	10	Cassano et al. (2001)
	7.7		11.9		8.6		3.6		5		Tunay et al. (1995)
T [°C]	10	30	10	25	20	35	–	–	20	60	Cassano et al. (2001)
BOD_5	2000	5000	5000	20,000	1000	4000	100	250	6000	15,000	Cassano et al. (2001)
COD [mgL^{-1}]	3000	6000	–	–	–	–	1000	3000	–	–	Sundarapandiyan et al. (2010)
	5000	11,800	20,000	40,000	2500	7000	800	400	15,000	75,000	Cassano et al. (2001)
	31,000		58,000		5325		2900		4365		Tunay et al. (1995)
TSS [mgL^{-1}]	25,000	40,000	–	–	–	–	30,000	70,000	–	–	Sundarapandiyan et al. (2010)
	2300	6700	6700	25,000	2500	10,000	–	–	–	–	Cassano et al. (2001)
TDS	22000	33000	–	–	–	–	29000	67000	–	–	Sundarapandiyan et al. (2010)
Cl^- [mgL^{-1}]	15000	30000	–	–	–	–	20000	30000	–	–	Sundarapandiyan et al. (2010)
	17,000	5,0000	3300	25,000	2500	15,000	8950	2000	5000	10,000	Cassano et al. (2001)
Sulfides	0	700	2000	3300	25	250	–	–	–	–	Sundarapandiyan et al. (2010)
	–		2670		134		–		–		Tunay et al. (1995)
Cr (III) [mgL^{-1}]	–	–	–	–	–	–	–	4100	0	3000	Cassano et al. (2001)
NH_3-N [mgL^{-1}]	850		380		3800		670			530	Tunay et al. (1995)

3.2.3. Wetlands and ponds

Tadesse et al. (2004) reported the influence of pH, temperature and dissolved oxygen in a pilot-scale advanced integrated wastewater pond system (AIWPSs) treating tannery effluent. According to their studies a combination of advanced facultative pond (AFP), secondary facultative pond (SFP) and maturation pond (MP) all arranged in series, preceded with simple pretreatment can adequately treat raw combined tannery wastewater.

Constructed wetlands (CWs) may be an interesting treatment option for leather tannery wastewater. Several efforts have been undertaken in the last decade for selecting plant species tolerant to this peculiar wastewater (Mant et al., 2004; Calheiros et al., 2007, 2008, 2012), selecting suitable supporting media or substrate (Calheiros et al., 2008) and for approaching the bacterial dynamics (Aguilar et al., 2008; Calheiros et al., 2009a,b).

The choice of plants plays an important role in CWs, as they must survive the potential toxic effects of the wastewater and its variability. The potential of CWs for the phytoremediation of chromium (10 and 20 $mgCrdm^{-3}$) from primary treated leather tannery wastewater by *Penisetum purpureum*, *Brachiaria decumbens* and *Phragmites australis* has been investigated by Mant et al. (2004). Calheiros et al. (2008) evaluated the use of *Canna indica*, *Typha latifolia*, *P. australis*, *Stenotaphrum secundatum* and *Iris pseudacorus* in CWs receiving wastewater from a tannery production plant, under two different hydraulic loading rates, 3 and 6 cm d^{-1}. *P. australis* and *T. latifolia* were the only plants that were able to establish successfully. The same authors (Calheiros et al., 2012) tested *Arundo donax* and *Sarcocornia fruticosa* in two series of horizontal subsurface flow CWs used to treat the effluent of conventional biological treatment system operating at a tannery site. According to their results a high efficiency in removing COD (51 and 80%) and BOD_5 (53 and 90%) for COD inlet: 68–425 mgL^{-1} and for BOD_5 inlet: 16–220 mgL^{-1} could be observed. A more recent study carried out by Dunn et al. (2013) have demonstrated the technical viability in the use of tannery effluent as a growth medium for *Arthrospira* (*Spirulina*). Finally according to Dotro et al. (2012) chromium can be retained in wetlands with non-specialized media.

3.3. Emerging treatment technologies

3.3.1. Membrane processes

In recent years membrane technologies have been focused on and their cost is continuing to reduce while the application possibilities are ever extending. The use of membrane technologies applied to the leather industry represents an economic advantage, especially in the recovery of chromium from residual waters of leather tanning. Several studies showed as crossflow microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and supported liquid membranes (SLMs) can be applied in leather industry for the recovery of chromium from spent liquors (Fabiani et al., 1996; Ashraf et al., 1997; Cassano et al., 2001; Labanda et al., 2009), the reuse of wastewater and chemicals of the deliming/bating liquor (Gallego-Molina et al., 2013), the reduction of the polluting load of unhairing and degreasing (Cassano et al., 1997; De Pinho, 2009; Wang et al., 2011), the removal of salts and in the biological treatment of tannery effluents in the light of their reuse.

Reverse osmosis (RO) with a plane membrane has been used as post treatment to remove refractory organic compounds (chloride and sulphate) by De Gisi et al. (2009). The high quality of the permeate produced by the RO system with a plane membrane allowed the reuse of the tannery effluent within the production cycle, thus reducing groundwater consumption.

3.3.2. Membrane bioreactors

Membrane Bio-Reactor (MBR) has been attracting much attention from scientists and engineers for tannery wastewater treatment due to the numerous advantages over conventional activated sludge process (CASP) such as elimination of settling basins, independence of process performance from filamentous bulking or other phenomena affecting settleability (Munz et al., 2008; Suganthi et al., 2013). The separation of biomass from effluent by membranes also allows the concentration of mixed liquor-suspended solids (MLSS) in the bioreactor to be increased significantly. However from the studies of Munz et al. (2009) it is possible to infer how the kinetics of nitrification are effectively reduced by the presence of tannins, without large differences between biomass selected with either the CASP and the MBR. One of the main drawbacks of membrane application is a significant fouling due to the clogging, adsorption and cake layer formation by the pollutants onto the membrane. In recent years extensive work is in progress to reduce the bio-fouling. One such mitigation is the hybrid membrane bioreactor (HMBR) that is originated, where membrane technology is integrated with various treatment technologies, see the section Hybrid processes.

3.3.3. Advanced oxidation processes

There has been increasing number of studies on advanced oxidation processes (AOPs) to treat tannery wastewater and chemicals. AOP treatment uses strong oxidizing agents (O_3, H_2O_2) and/or catalysts (Fe, Mn, TiO_2) sometimes supported in activity by high-energy radiation, e.g., UV light (Schrank et al., 2004). These processes are all based on the production and utilization of hydroxyl radicals which are very powerful oxidants that quickly and unselectively, oxidize a broad range of organic compounds. The scientific interest towards AOPs application to high strength wastewater has increased remarkably in the past 20 years. Table 5

Table 3
Characteristics of tannery wastewater. Conducibility is expressed as[μmho/cm] all other parameters as [mgL^{-1}].

pH	Cond.	COD	BOD_5	TSS	TS	SS	TDS	Alk.	Chloride	Sulphate	Suplhide	NH_4-N	Phosph	Cr	Iron	References
8.4	–	4947	–	2239	–	–	–	665	7601	–	–	95	4	–	–	Ates et al. (1997)
10.5	–	3114	1126	–	18,884	1147	17,737	–	–	–	55	33		83	–	Ram et al. (1999)
7.79	–	2155		–		915		–	–	–	35.8	168		50.9	–	Orhon et al. (2000)
7.5-9	–	5000–10,000	1500–2000	–	–	–	–	–	–	–	–	–	–	100	–	Song et al. (2000)
8	–	1803	106	526			9435		2251			70			–	Dantas et al. (2003)
-	–	8000	930			2004	15,152	–	–	–	228			11.2	–	Koteswari and Ramanibai (2003)
7.4	–	2227	1800	578					3430	1210		137			–	Cotman et al. (2004)
8.2-8.5	–	5650	–	–	19,775	5025	14,750	–	–	–	–	–	–	–	–	Thanigavel (2004)
10.72	–	11,153	2906	–	–	–	6810	–	–	–	507	162		32.87		Leta et al. (2004)
7.7	–	2200				5003	36,800	–	–	–	–	–	–	–	–	Lefebvre et al. (2006)
7.7	–	2426	–	–	–	–	–	–	–	–	286	335		29.3		Szpyrkowicz et al. (2005)
6.6	8600	6855	2700	2865				1010	2835	745		70.5		140		Lofrano et al. (2006)
7.08	–	–	–	–	10,265	2820	–	–	–	–	–	128		90-100		Ganesh et al. (2006)
7.2	19,950	2810	910	1520	–	–	–	–	6400		89	130		62	0.62	Kurt et al. (2007)
8.3	–	3100		1195	–	–	–	1010	4150	–	–	54	–	–	–	Karahan et al. (2008)
7.08-8.7	–	4100–6700	630–975			600–955	13,300–19,700	–	–	–	–	–	–	11.5-14.3		Kongjao et al. (2008)
7.2	–	2102		576	–	–	–	–	3260	–	–	118	–	–	–	Munz et al. (2009)
7.9-9.2	20,042	2533	977	1244	–	–	21,620		6528		860	118	62	258	2.56	Mandal et al. (2010)
7.4	–	3700	1470			2690	–	–	–	–	440	180	–	–	–	Apaydin et al. (2009)

Cond.: conducibility; COD: Chemical Oxygen Demand; BOD: Biochemical Oxygen Demand; Alk.: alkalinity; TS: Total Solids; TSS: Total Suspended Solids; SS: Suspended Solids; TDS: Total Dissolved Solids; Phoph.: phosphorous.

summarizes findings of various AOPs applied to tannery wastewater and chemicals. Although most studies evaluated the efficiency of the treatment by COD removal, TOC remains more suitable parameter to investigate the state of mineralization occurring in the processes (Schrank et al., 2004, 2005; Costa et al., 2008; Monteiro Paschoal et al., 2009).

3.3.3.1. Fenton based processes. Fenton oxidation (FO) is achieved by the reaction of H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions which are among the most common homogeneous systems and potential sources of hydroxyl radicals generation (Gogate and Pandit, 2003). The key features of the Fenton oxidation are believed to be its reagent conditions, like [Fe^{2+}], [Fe^{3+}], [H_2O_2] and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents) (De Laat et al., 2004; Meriç et al., 2005). The $Fe^{2+}/Fe^{3+}/H_2O_2$ system exhibits its maximum catalytic activity at pH = 2.8–3.0 (Lofrano et al., 2007a). At elevated pH (>5), the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of Fe^{3+} with H_2O_2 is inhibited (Kuo, 1992).

The low pH, relatively high temperature (43–45 °C) and the high presence of aromatic compounds, especially in the streams of re-tanning baths are attractive to use FO processes (Lofrano et al., 2007a, b, 2010a)

3.3.3.2. Photo oxidation processes. Ultraviolet photolysis (UV) applied to the untreated tannery wastewater did not change the parameters COD, TOC and toxicity to *D. magna* (Schrank et al., 2004).

Because the efficiency of photolysis of some organics was proved depending on their reactivity and photosensivity (Kusic et al., 2006) it can be supposed that the organic structure of leather tanning wastewater as well as of some tanning agents are not proper to be destroyed by UV alone. In fact, no effect of UV radiation on solution of syntans was observed in the experiments of Lofrano et al. (2007b). The formation of intermediate components which can affect the color removal has to be seriously taken into account. Some studies reported an increase of color after photolysis due to the cleavage of the dye chromophore Pokrywiecki Sauer et al. (2006) which carried out photo oxidation test on coagulated tannery wastewater (see Table 5) observed as although COD and UV_{254} decreased progressively during the oxidation time, the color intensity of treated wastewater increased.

To be effective, photolysis requires strong UV-light with a short wavelength (<400 nm) and chemical oxidants such as hydrogen peroxide and ozone. Hydrogen peroxide is readily photolyzed to produce HO• radicals. However, as most studies proved, the effect of hydrogen peroxide is dependent on the characteristics of the wastewater (type and concentration of organic compounds, pH, presence, temperature of wastewater and type of inorganic ions), the concentration of oxygen in the solution, the

Table 4
Reported results on COD fractionation of tannery wastewater.

Reference	CT1 [mgL^{-1}]	ST1 [mgL^{-1}]	SS1 [mgL^{-1}]	SH1 [mgL^{-1}]	XS1 [mgL^{-1}]	SI1 [mgL^{-1}]	XI1 [mgL^{-1}]	SS1/CT1 %	SH1/CT1 %	XS1/CT1 %	SI1/CT1 %	XI1/CT1 %
Orhon and Ubay Cokgör (1997)	2410	1210	300	770	935	140	265	12.4	32	38.8	5.8	11
Orhon et al. (1998)	2300	1300	435	650	–	215	270	19	28.5	–	9.5	11.5
Orhon et al. (1999)	2284	1297	434	649	724	214	263	19	28.4	31.7	9.4	11.5
Ganesh et al. (2006)	1912	1912	346	800	303	462	–	18.1	41.8	15.8	24.2	–
Karahan et al. (2008)	3100	1240	230	615	240	395	1620	7.4	19.8	7.7	12.7	52.2
Insel et al. (2009)	2368	1018	355	474	1089	189	260	15	20	46	8	11
Munz et al. (2008)	3690	–	–	–	–	–	–	22	20	27	20	11

Total COD (CT) and soluble COD (ST) in the influent. Readily biodegradable COD (S_{S1}); rapidly hydrolysable fraction (S_{H1}); slowly hydrolysable COD fraction (X_{S1}) in the influent total COD. Soluble inert COD (S_{I1}), the particulate inert fraction (X_{I1}) of the influent COD.

Table 5
Chemical oxidations and AOP_S applications to tannery wastewater.

Authors	Wastewater characteristics	COD influent [mgL^{-1}]	AOPS	Type of equipment and experimental details	Highlights of the work
Schrank et al. (2004)	Coagulated/ Flocculated tannery wastewater.	2365	Ozone	*Plant description (1)* The gas was fed into reactor using a sintered glass plug located at the bottom of the reactor while the wastewater was thoroughly mixed by stirring. *Operational conditions* pH 3–7–11 O_3 flow rate 2.6 gO_3 h^{-1} t: 60 min	17% of COD removal 12% of TOC removal 24% of BOD removal pH 11
Dogruel et al. (2004)	Settled tannery wastewater (STW) Biologically treated tannery wastewater (BTW)	1785 835	Ozone	*Plant description (1)* Ozonation was carried out in a 1.5 L semi-batch bubbled gas washing bottle reactor with an effective depth of 23 cm. Ozone gas was supplied at the bottom of the reactor through a sintered glass plate diffuser. *Operational conditions* O_3 flow rate 21.6, 42.8, 59.9, 76.0, 93.6 mg min^{-1} t: 5–10–15–10 min.	STW 6% of COD removal t 5 min ozone flow-rate of 42.8 mg min^{-1}. BTW 30% of COD removal t 5 min ozone flow-rate of 42.8 mg min^{-1}.
Srinivasan et al. (2009)	Syntethic solution of leather dye	30–65–180–360	Ozone	*Plant description (1)* Ozonation was carried out in a cylindrical glass reactor of 5 L capacity (8.5 cm diameter and height 125 cm). *Operational conditions* pH 4–7–9–11 Applied O_3 dose 1.6 mgL^{-1} t: 10–20–30–40–50 min	Maximum decolorization greater than 97% can be achieved for all concentrations of dye studied t 20 min pH 7
Preethi et al. (2009)	Raw tannery wastewater RTW Diluted RTW (dRTW) Dye synthetic solution	5000 2000 300	Ozone	*Plant description (1)* The schematic of the experimental set-up consisted of an acrylic cylindrical column (2.5 cm internal diameter and 30 cm height packed with glass beads of 5 mm diameter) feed up with a mixture of oxygen/ozone introduced through a porous diffuser plate placed at the bottom of the column. *Operational conditions* pH 4-7-11 O_3 flow rate 2×10^{-3}, 4×10^{-3}, 6×10^{-3} m^3 min^{-1} t: 20–120 min	dRTW 60% COD removal RTW 20% COD removal pH 11 t 80 min O_3 flow rate: $6 \times 10 - 3$ m^3 min^{-1}.
Di Iaconi et al. (2010)	Biologically treated tannery wastewater	2900	Ozone	*Plant description (2)* Sequencing Batch Biofilter Granular Reactor (SBBGR) equipped with an ozonation unit. A pump extracted the biologically treated wastewater from the SBBGR (at a flow rate of 2 m^3h^{-1}) and drove it through an ozone reactor (volume: 0.25 m^3) Finally, the ozonated wastewater came back to the SBBGR for the final biological degradation. *Operational conditions* Applied O_3 dose 150 g m^{-3} t: 60 min	97% of COD removal 96% of TSS removal 91% of TKN removal 98% of surfactants removal 96% of color removal
Houshyar et al. (2012)	Pre-alkalized tannery wastewater	2177	Ozone	*Plant description (1)* Ozonation experiments were conducted in a cylindrical glass of 3 L capacity (i.d. = 70 mm). *Operational conditions* pH 3, 6, 9 Ozone flow rate 1 and 8 g h^{-1}. t:10, 20, 40, 60, 90 and 120 min T 27 °C	COD removal from 30% to 70% after 120 min when ozone flow rate increased from 1 to 8 g/h.
Panizza and Cerisola (2004)	Synthetic tannery wastewater	2080	Electrochemical treatment	*Plant description (1)* The electrolyses were performed in a one-compartment flow cell under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. Lead dioxide (Ti/PbO_2) and mixed titanium and ruthenium oxide ($Ti/TiRuO_2$) electrodes. *Operational conditions* pH 5, 6.5, 10	Both electrodes rapidly oxidized the tannic acid in the first 2 h of treatment. PbO_2 gave faster COD removal than $Ti/TiRuO_2$. Although the $Ti/TiRuO_2$ required almost the same energy consumption for complete COD removal, it was more stable and did not release toxic ions, so it was the best candidate for industrial applications

(continued on next page)

Table 5 (*continued*)

Authors	Wastewater characteristics	COD influent [mgL^{-1}]	AOPS	Type of equipment and experimental details	Highlights of the work
				T 20–30–40–50 °C Current density: 300–600 A m^{-2} t: 0.3–1–2–3–4–5–6 h	
Kurt et al. (2007)	Raw tannery wastewater	2810	Electrochemical treatment	*Plant description (1)* Experimental studies were performed in a batch laboratory reactor consisting of a 0.5 L glass beaker equipped with a cathode and an anode, both made of iron and installed in parallel. The total effective electrode area was 45.0 cm^2. *Operational conditions* pH 3.0, 5.0, 7.2 H_2O_2 840, 1670, 3340, and 5010 mgL^{-1} Electrical power 1.2, 4.0, and 15.0 W	70% of COD removal 840 $mgL^{-1}H_2O_2$ Electrical power of 15.0 W, t 10 min pH 3. In neutral pH with 1670 mg/l oxidant dose and 15.0 W, 58% COD removal was obtained in 10 min.
Costa et al. (2008)	Equalized tannery wastewater	TOC 1005	Electrochemical treatment	*Plant description (1)* 50 mL one-compartment cell $Ti/Ir_{0.01}Sn_{0.99}O_2$, $Ti/Ir_{0.10}Sn_{0.90}$ O_2, $Ti/Ru_{0.10}$ $Sn_{0.90}$ O_2, $Ti/Ru_{0.30}$ $Ti_{0.70}$ O_2, $Ti/Ir_{0.15}$ $Ru_{0.15}$ $Sn_{0.70}$ O2, and $Ti/Ir_{0.30}$ $Ti_{0.30}$ $Sn_{0.40}$ O_2 electrodes. Total surface area of the electrodes: 62,500 cm^2 Distance between the cathodes and anodes:1 cm *Operational conditions:* Current density: 20–100 $mAcm^{-2}$	82.6% phenol removals at 20 $mAcm^{-2}$, 78.5% at 50 $mAcm^{-2}$, and 83.9% at 100 $mAcm^{-2}$, after 5 h of electrolysis. After 5 h of electrolysis, TOC removals are 14.3, 31.3, and 40.5% at 20, 50, and 100 $mAcm^{-2}$,
Ayhan Sengil et al. (2009)	Tannery liming drum wastewater	25,300	Electrochemical treatment	*Plant description (1)* Plexiglass electrolytic reactor 1150 mL. Iron electrodes consisting of pieces of sheet mild steel or aluminum. (9.3 cm × 7.5 cm × 0.3 cm). *Operational conditions* pH 2–11, Current density 3.5–70 A cm^{-2} t: 10–70 min	Aluminium electrodes: 62% COD removal pH 3–5 Mild steel electrodes: 82%, COD removal Current density 35 mA cm^{-2}, t 10 min electrolysis time pH 3
Espinoza-Quinones et al. (2009)	Equalized Tannery wastewater	17,618 12,225	Electrochemical treatment	*Plant description (1)* Polyethylen electrolytic reactor: 20.5 cm diameter, 30 cm, 5 L working volume. Electrodes of iron plates: 7 cm width, 14 cm height, and 0.15 cm thickness. Active electrode surface area: was 80.5 cm^2 (7 cm × 11.5 cm) with a 4.0 cm gap between them. *Operational conditions* Currents and voltages ranging from 0 to 10A and from 0 to 30 V pH 6.5 7.0 7.5 8.0 8.5 9.0 t: 30–45 min	51–56% COD removal 30–70% TSS removal >98% Cr removal >96% Turbidity removal
Sundarapandiyan et al. (2010)	Synthetic tannery wastewater (STW) Pickling wastewater (PW)	10,715 9520	Electrochemical treatment	*Plant description (1)* Plexiglass electrolytic reactor 2 L working volume Cylindrical graphite electrodes (diameter 2.54 cm; length 13 cm) Total surface area of the electrodes 427.84 cm^2. *Operational conditions* pH 3–9 Current density 0.006–0.024 A cm^{-2} Salt concentration 10-40 g/l NaCl t: 120 min	STW: 89% COD removal PW: 79% COD removal current density 0.012, A cm^{-2} pH 9 salt concentration 30 gL^{-1} NaCl
Módenes et al. (2012)	Tannery wastewater treated by photo-Fenton	1188	Electrochemical treatment	*Plant description (1)* 1.5 L cylindrical glass container Aluminum plates electrodes (7.5 cm, 12.12 cm, 0.17 cm) with a 4.0 cm gap between them *Operational conditions* pH 8.3 Current density 68 mA cm^{-2} Currents and voltages, ranging from 0 to 10 A and from 0 to 30 V t: 5–60 min	After 15 min strong reductions on Cr and Fe concentrations were attained, reaching 0.24 and 3.16 mg L^{-1}, respectively, which are below the limits recommended by the Brazilian environmental norm for discharge of wastewater into freshwater bodies.
Dantas et al. (2003)	Raw tannery wastewater	1803	Fenton	*Plant description (2)* Reactor volume 500 ml *Operational conditions* pH 2.5–T 25 °C	70% COD removal t 20 min 90% COD removal t 240 min.

Table 5 (*continued*)

Authors	Wastewater characteristics	COD influent [mgL^{-1}]	AOPS	Type of equipment and experimental details	Highlights of the work
				Fe^{2+} 1 g L^{-1}–H_2O_2 15 gL^{-1} t: 20–240 min	
Schrank et al. (2005)	Coagulated/ diluted tannery wastewater	130	Fenton	*Plant description (1)* A 15 W medium pressure mercury lamp surround by a quartz thimble, was used as UV source. Reactor volume 2000 ml *Operational conditions* $FeSO_4$ $7H_2O$ 50–240 mgL^{-1} H_2O_2 100–500 mgL^{-1} t: 2 h	H_2O_2/Fe^{2+} 500/100 w/w 80% COD removal.
Lofrano et al. (2007a)	Synthetic solution of tanning agents: synthetic tannins (ST) and oils (OL)	ST: 300 OL: 300	Fenton	*Plant description (1)* Reactor volume 500 ml *Operational conditions* pH 3–3.5 H_2O_2 600 mgL^{-1} $FeSO_4$ 400–750 mgL^{-1} T 40–45 °C	ST: $H_2O_2/FeSO_4$ 600/500 (w/w) pH 3 – T 40 °C 80–90% of COD removal OL: $H_2O_2/FeSO_4$ 600/750 (w/w) pH 3–T 43 °C 95% of COD removal t 30 min
Lofrano et al. (2010b)	Synthetic solution of degreasing agent (EP) Effluent of the first phase (degreasing) of re-tanning bath (DGW)	350 6300	Fenton	*Plant description (1)* Reactor volume 500 ml *Operational conditions* pH 3 T 40–45 °C H_2O_2 0.15–0.6 gL^{-1} $FeSO_4$ 500–750 mgL^{-1} t: 0–30 min	68% of COD removal $H_2O_2/FeSO_4$ 600/750 w/w. t 30 min
			Fenton	*Plant description (1)* Reactor volume 500 ml *Operational conditions* pH 3 T 40–45 °C H_2O_2 600 -1200 $FeSO_4$ 750–1000 w/w. t: 0–30 min	$H_2O_2/FeSO_4$ 600/1000 (w/w) 72% COD removal 86% UV_{254} and 77%, UV_{280} No toxicity removal up to 75% and 87.5% dilution.
Schrank et al. (2004)	Coagulated/ Flocculated tannery wastewater.	2365	Photocatalysis (UV/TiO_2)	*Plant description (1)* Reactor volume 2 L 15 W medium pressure mercury lamp *Operational conditions* pH 3,7,11 TiO_2 1 gL^{-1} t: 2 h	6% COD removal—pH 3 11% TOC removal—pH 3 15% BOD removal—pH 7
Schrank et al. (2005)		130 mgL^{-1}	(UV/H_2O_2)	*Plant description (1)* A 15 W medium pressure mercury lamp surround by a quartz thimble, was used as UV source. *Operational conditions* pH 3, 7, 11 H_2O_2 200–1000 mgL^{-1}. T 28 °C	Optimum results in terms of TOC removal (>50%) were achieved after 2 h of treatment at pH 3 and an initial hydrogen peroxide concentration of 400 mgL^{-1}. No changes were observed in the TOC elimination rates between pH 7 and pH 11.
Pokrywiecki Sauer et al. (2006)	Coagulated tannery wastewater 200–800		UV/H2O2	*Plant description (1)* Reactor volume 2 L 80 W high-pressure mercury vapor lamp Light intensity 1.64 × 10^{-4} Einstein min^{-1}. *Operational conditions* H_2O_2 0.3, 0.6, 0.9, 1.8 gL^{-1} pH 2.5 t: 0–3 h	60% COD removal 4 h H_2O_2 0.5 gL^{-1}
			Photocatalysis (UV/TiO_2)	*Plant description (1)* Continuous system constituted by an annular reactor 15 W UV-lamp (300–410 nm, maximum emission at 355 nm). *Operational conditions* pH 2.5 TiO2 1 gL^{-1}. t: 0–3 h	19–66% COD removal 0–92% BOD removal t 1 h
Lofrano et al. (2007b)	Synthetic solution of synthetic tannins (ST)	300	Photo-Fenton ($UV/Fe^{2+}/H_2O_2$)	*Plant description (1)* Reactor volume 2 L UV-C lamp 16 W low-pressure mercury vapor lamp (254 nm) UV-A black fluorescent lamp 125 W (365 nm)	$H_2O_2/FeSO_4$ 300/750 (w/w) After 15 min of oxidation by PF-A and PF-C the COD removal efficiency of initial 300 mg/l equivalent of ST was 78% and 76% respectively

(*continued on next page*)

Table 5 (*continued*)

Authors	Wastewater characteristics	COD influent [mgL^{-1}]	AOPS	Type of equipment and experimental details	Highlights of the work
				Operational conditions: pH 3 T 40–45 °C H_2O_2 0.3–0.6 gL^{-1} $FeSO_4$ 150-750 mgL^{-1} t 0–30 min	
Monteiro Paschoal et al. (2009)	Synthetic solution ofleather acid dye (acid red 151) and anionic surfactant, Tamol®,	0.005% (m/v) acid 151 dye + 0.009% surfactant + 14.12 mgL^{-1} Cr(VI) in 0.1 mol L^{-1} Na_2SO_4	Photo-Electrochemical treatment	*Plant description (1)* Reactor volume 250 ml Working electrode of TiO_2 acting as anode (12 cm^2), Auxiliary electrode of pt gauze and Reference electrode Ag/AgCl UV light source (315–400 nm) from a 125 W medium pressure mercury lamp ($I = 9.23 Wm^{-2}$) *Operational conditions* pH 2 t: 0–60 min	The best experimental conditions were found to be pH 2.0 and 0.1 mol L^{-1} sodium sulfate when the nanoporous Ti/TiO_2 photo anode was biased at +1.0 V and submitted to UV-irradiation. 100% discoloration 98–100% of Cr(VI) removal 95% TOC removal
Módenes et al. (2012)	Equalized Tannery wastewater	11,878	Photo-Fenton ($UV/Fe^{2+}/H_2O_2$)	*Plant description (1)* Reactor volume 500 mL External environment for 5 hr of solar irradiation on non-cloudy days, during summer *Operational conditions* Fe^{2+} 0.4 to 0.5 g L^{-1} H_2O_2 15 to 30 g L^{-1} pH 3 t: 2 h	0.4 g L^{-1} Fe^{2+} and 15 g L^{-1} H_2O_2 540 min of irradiation time 90% COD removal 50% TSS removal

(1) Experiments were conducted at lab scale; (2) Experiments were conducted at pilot scale.

intensity and wavelength of the UV light, the desirable extent of treatment and the concentration of hydrogen peroxide (Pokrywiecki Sauer et al., 2006) (see Table 5).

A combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion, the so-called photo-Fenton process produces more hydroxyl radicals in comparison to the conventional Fenton method (Fe^{2+} with hydrogen peroxide) or to the photolysis (Gogate and Pandit, 2004). The reason for the positive effect of UV light on the degradation rate include the photolysis of Fe^{3+} that leading to the production of HO• and Fe^{2+}. Moreover, •OH are also produced via direct H_2O_2/UV-C photolysis (slow reaction) and the reaction of H_2O_2 with Fe^{2+} produced by photoreduction of Fe^{3+}(Lofrano et al., 2010a,b).

3.3.3.3. Ozone based processes. The important operating parameters for the ozonation can be given as: pH of the system (hydroxyl radicals are formed from ozone decomposition at higher pH, while the molecular ozone remains as the main oxidant at low pH values), ozone partial pressure, contact time and interfacial area, operating temperature, presence of catalyst (Gogate and Pandit, 2004).

Ozonation prior to biological treatment is widely carried out in order to achieve high color removal efficiencies and convert refractory organics to biodegradable organic compounds. The biodegradability index of the tannery effluent has increased from 0.18 to 0.49 during ozonation (Preethi et al., 2009). However, with pre-ozonation, it should be kept in mind that ozone can also oxidize the biodegradable fraction of influent COD. Since ozonation competes with biological treatment under these conditions this is an undesirable result that must be checked beforehand (Dogruel et al., 2006). Schrank et al. (2004) observed that O_3 reduced toxicity of tannery wastewater. This decrease of toxicity was observed in parallel with the destruction of the aromatic surfactant homologues of nonylphenolethoxylate type. However Schrank et al. (2009) also reported that although *Vibrio fischeri* and *D. magna* toxicity tests performed in parallel displayed a decrease in toxicity after O_3 treatment, the estrogenic activity determined by enzyme linked receptor assay (ELRA), controversially, showed increase in concentration of endocrine disruptors compounds (EDCs).

Alternative procedures involving ozonation catalyzed with H_2O_2, Fe^{2+}, UV light, and TiO_2 allow a quicker removal of organic pollutants, because such catalysts improve the oxidizing power of O_3 as described in the following equations:

$$O_3 + H_2O_2 \rightarrow OH\bullet + O_2 + HO_2\bullet \quad (1)$$

$$Fe^{2+} + O_3 \xrightarrow{hv} FeO^{2+} + O_2 \quad (2)$$

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \quad (3)$$

The application of O_3/UV achieves the highest degradation and oxidation rates at alkaline pH. UV radiation induced the generation of free radicals. Thus, ozone under UV radiation reacted with the substances contained in the tannery wastewater by an indirect reaction pathway involving free radicals.

3.3.3.4. Photocatalysis. The operating parameters of photocatalytic oxidation process, are amount and type of the catalyst, wavelength of the irradiation, reactor design, organic content of the effluents, temperature, pH, radiant flux, aeration, effect of ionic species. A major advantage of this process is the possibility to effectively use sunlight or near UV light for irradiation, which should result in considerable economic savings especially for large-scale operations (Gogate and Pandit, 2003). Few studies focused on photocatalysis application to leather tannery wastewater (Schrank et al., 2004; Pokrywiecki Sauer et al., 2006). Authors observed an increase of the toxicity to *D. magna* (Schrank et al., 2004) and *Artemia salina* (Pokrywiecki Sauer et al., 2006) after UV/TiO_2 treatment, despite the high COD removal (Pokrywiecki Sauer et al., 2006).

3.3.3.5. Electrochemical treatment. Using electricity to treat water was first proposed in UK in 1889. Since the early 1960s, electrochemical reactors were used for the recovery of pollutants from metal plating factories (Szpyrkowicz et al., 2001). Despite the common approach for its expensive capital costs, nowadays, electrochemical technologies

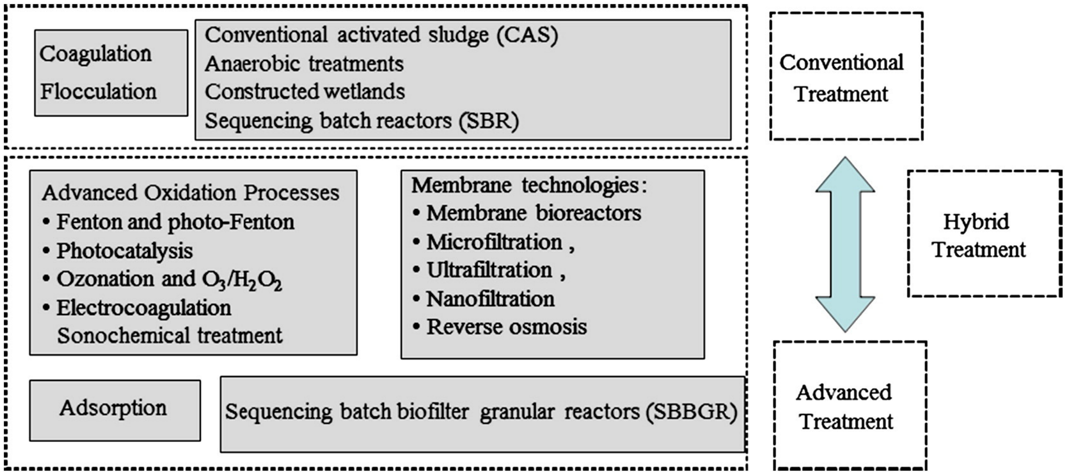

Fig. 5. Schematic diagram of the progress of the treatment strategies used for tannins wastewater treatment.

have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact (Sundarapandiyan et al., 2010). The electrochemical oxidation can be achieved by both the direct and indirect processes and the effectiveness of this process strongly depends on the treatment conditions and on the nature of the electrodic materials (Costa et al., 2008). The presence of high concentrations of salts, mainly chlorides, makes the tannery wastewater particularly amenable for electrochemical purification, offering the possibility to couple both direct and indirect electro-oxidation (Szpyrkowicz et al., 2001; Costa et al., 2008; Sundarapandiyan et al., 2010). Application of different anodic materials with different electrocatalytic properties can affect reactor treatment efficiencies (Panizza and Cerisola, 2004; Costa et al., 2008) (see Table 5).

The kinetics of the electrochemical process have been found up to 100-fold faster than biological oxidation process (Szpyrkowicz et al., 2001). Ammonia (Rao et al., 2001; Min et al., 2004) and nitrite (Lin and Wum, 1996) were successfully removed by electro treatment as well as many other compounds such as benzoquinone, benzene (Fleszar and Ploszynska, 1985), phenols (Costa and Olivi, 2009), chlorophenols, dyes (Martınez-Huitle and Brillas, 2009), formaldehyde (Do and Yeh, 1995). However electrochemical oxidation proved uneconomic when applied to raw tannery wastewaters due to the very high energy requirement. Whereas the process was found to be competitive in costs of operation and treatment efficiency when applied as a final polishing step or as a substitute for biological nitrification and denitrification. In this case, the volume of the reactor is 15/20 times smaller than a nitrification/denitrification unit and the removal of nitrogen can be achieved at about 15 k Wh m^{-3} of wastewaters containing ammonia at concentrations of 10 mol m^{-3} (Szpyrkowicz et al., 2001).

Electro Fenton (EF) is an electrochemical treatment application that includes the combined advantages of Fenton and electrochemical processes. Kurt et al. (2007) obtained an effluent complying with the Discharge Limit set by the Water and Sewerage Administration of Istanbul (COD 800 mgL^{-1}) treating raw tannery wastewater by EF. According to their studies, 99.5% of the sulphides removal was achieved within the first 15 min. The same authors underlined that COD reduction changed from 41% to 99% based on different variables such as wastewater type, electrical energy consumption, reaction time, etc.

4. Discussion and Outlooks

4.1. AOPs application to tannery chemicals and wastewater

When AOPs are applied on tannery wastewater some drawbacks have to be taken into account. The presence of scavenger compounds can reduce the kinetics of the reactions up to do uneconomical the processes. Since the tannery wastewater contain appreciable amounts of chromium is highly recommended to evaluate the possible effects of the oxidation on the transformation of chromium atoms in different oxidation states (Dogruel et al., 2006). The oxidation of trivalent chromium transforming to chromium VI that is well known to be more toxic than the previous one which the case to be avoided (De Laat et al., 2004). For these reasons AOPs should be applied more properly to segregated effluents containing for example high amount of aromatic compounds for Fenton treatments or high content of salts for electrotreatment.

According to Table 5 most of studies have been carried out at bench scale. There has not been yet full scale application of those emerging technologies using advanced oxidation although some of them proved good achievements to remove xenobiotics present in tannery wastewater.

The following issues are to be underlined during application of AOPs to leather tannery.

4.1.1. Catalysts/oxidant ratio

Although the AOPs reactions have been widely studied there is no agreement on the ratio $[H_2O_2]/[Fe^{2+}]$ or ozone dose which gives the best results as the tannery wastewater compositions are variable. The same occurs with H_2O_2 based reactions, where an excess of H_2O_2 can act as a hydroxyl scavenger instead of hydroxyl radicals source and which in addition interferes with the determination of the chemical oxygen demand (COD) (Kang, 2002). According to Mandal et al. (2010) there was only 1.7 time increase in %COD reduction by Fenton oxidation increasing the H_2O_2 dose about 2.3 times.

4.1.2. Organic loading

The initial effluent concentration has a significant impact on the behavior of examined AOPs. Preethi et al. (2009) reported that the ozonation efficiency in terms of COD removal was reduced from 60% to 20% when the effluent COD concentration increased from 2000 to 5000 mgL^{-1}.

4.1.3. The effect of pH

The initial pH of wastewater influences the reaction mechanism of ozone, Fenton reaction and the stability of hydrogen peroxide. Fenton oxidation is not effective at pH values higher than 4.0 because Fe^{2+} easily form Fe^{3+} form which has a tendency to produce ferric hydroxo complexes. Moreover, H_2O_2 is unstable and decomposing in basic ($pH > 9.0$) solutions (Kuo, 1992). On the contrary at alkaline condition the radical oxidation of ozone is favored (Gogate and Pandit, 2004)

4.1.4. Transformation products and toxicity

As stated by several studies (Lofrano et al., 2007b; Schrank et al., 2009) although high COD is achieved, the GC-MS spectral analyses of treated solutions can display a number of intermediates. The presence of oxidation by-products at the end of the Fenton and Photo-Fenton treatment (Lofrano et al., 2007b) seems to be unavoidable and makes a toxicity assessment necessary.

4.1.5. Pretreatment requirement

The optimum allocation of AOPs application in wastewater treatment plant needs to be properly evaluated. For highly polluted wastewaters pre-treatment is required prior to the application of AOPs (Schrank et al., 2004).

4.1.6. Hybrid processes

In order to overcome the possible disadvantage of pre-ozonation, a combined treatment scheme of biological treatment + ozonation + biological treatment can be applied. In such a treatment, by the first biological treatment easily biodegradable COD can be removed. The following ozonation then serves as a mid-treatment process to ease further biological treatment by either chemically converting the inert COD to biodegradable forms and/or increasing the rates of biodegradation of organics (Dogruel et al., 2006; Di Iaconi et al., 2010; Di Iaconi, 2012; Houshyar et al., 2012). More recently Suganthi et al. (2013) evaluated hybrid membrane bioreactor (HMBR) incorporating activated sludge process and electrocoagulation for the removal of COD and color in tannery wastewater. According to their studies the removals achieved by HMBR satisfied the dischargeable limit given by the Tamilnadu Pollution Control Board.

Furthermore Ayoub et al. (2011) attempted to use lime/bittern coagulation and activated carbon adsorption as a post treatment option for tannery wastewater. Meanwhile Munz et al. (2007) proposed a treatment scheme of powdered activated carbon integrated to MBR. There was another proposal using Chitin–humic acid hybrid as adsorbent for Cr (III) in effluent of tannery wastewater treatment (Santosa et al., 2008). The use of ground shrimp shells, not otherwise conditioned, as an adsorbent material to remove chromium(III) from tannery wastewater has been recently tested by Fabbricino et al. (2013). The reported removal efficiency was always over 90%, confirming the capacity of the tested materials to remove efficiently Cr (III).

Fig. 5 illustrates how those processes above mentioned can be integrated in sequence in practice.

4.1.7. Costs

Only few data are reported in the literature for AOPs overall costs due to their dependence on the effluent and plant characteristics. More interesting appear the comparison among overall cost of AOPs and more conventional treatment techniques. Table 6 reports a comparison of costs of various treatment options for leather tannery wastewater together with some specific pollutants which are mostly submitted to AOPs treatment. Depending on the scale of treatment option and wastewater characteristics (real or synthetic solutions) a wide range of variability in treatment costs is observed on Table 6.

When the biological degradation was integrated with ozonation for tannery wastewater treatment Di Iaconi et al. (2010) reported that residual concentration of COD much lower than the discharge limits of 160 mgL^{-1} were obtained. Furthermore the combined biological-ozonation treatment of tannery wastewater was characterized by a very low sludge production (0.1 kg of TSS/m^3 of treated wastewater) with interesting repercussions on treatment costs (0.9 € per m^3 of wastewater, including also the costs for the treatment and final disposal of sludge, Table 6). Tannery wastewater treatment carried out by conventional treatment consisting in a biological degradation followed by a Fenton treatment costs 3 times more (around 2.4 € per m^3) than a combined treatment with Sequencing Batch Biofilter Granular Reactor (SBBGR) and ozone, as estimated by Di Iaconi et al. (2010). Energy cost is the main and principal cost component in electro-oxidation. Sundarapandiyan et al. (2010) observed that the energy cost of electrochemical treatment of 1 m^3 of pickling tannery wastewater is 0.9 €.

An economical evaluation of membrane filtration has been reported by Scholz and Lucas (2003). The capital/operation costs of un-hairing liquor recovery with membrane filtration plant treating 23 m^3 per day, at 38LHM, consisting of 14 microfiltration cross flow modules corresponded to 3.6 € per m^3.

Table 6
Comparison of costs of various treatment options for leather tannery wastewater.

Influent wastewater	Plant description	Treatments schedule	Costs	References
Tannery wastewater	Bench scale	Chemically enhanced primary treatment		Haydar and Aziz (2009)
		• alum with cationic polymer	0.07 [€/m^3]	
		• alum with anionic polymer	0.08 [€/m^3]	
Tannery wastewater	Bench scale	Electrochemical treatment	1.64 [$/$m^3$]	Espinoza-Quinones et al. (2009)
Pickling wastewater	Bench scale	Electrochemical treatment	1.13 [$/$m^3$]	Sundarapandiyan et al. (2010)
Tannery wastewater	Bench scale	Photo Fenton	64.13 [$/$m^3$]	Módenes et al. (2012)[a]
		Electrochemical treatment	2.09 [$/$m^3$]	
		Photo-Fenton and EC	66.22 [$/$m^3$]	
Tannery wastewater	Pilot-plant	Activated sludge + Fenton	2.4 [€/m^3]	Di Iaconi et al. (2010)[a]
Tannery wastewater	Pilot-plant	SBBGR + Ozone	0.9 [€/m^3]	Di Iaconi et al., 2010[a]
Un-hairing liquor	Pilot plant	Ultrafiltration	3.6 [€/m^3]	Scholz and Lucas (2003)[b]
Butyric acid	Bench scale	CDEO	11 [€/m^3]	Canizares et al., 2009
		Ozonation	205 [€/m^3]	
		Fenton	35 [€/m^3]	
2-Propanol	Bench scale	CDEO	9 [€/m^3]	
		Ozonation	110 [€/m^3]	
		Fenton	71 [€/m^3]	
4-Chlorophenol	Bench scale	CDEO	13 [€/m^3]	
		Ozonation	114 [€/m^3]	
		Fenton	2 [€/m^3]	
2-Naphthol	Bench scale	CDEO	13 [€/m^3]	
		Ozonation	72 [€/m^3]	
		Fenton	7 [€/m^3]	
Eriochrome Black T	Bench scale	CDEO	35 [€/m^3]	
		Ozonation	99 [€/m^3]	
		Fenton	46 [€/m^3]	

[a] Including also the cost for the treatment and final disposal of excess sludge.
[b] Including the capital cost CDEO Conductive-Diamond Electrochemical Oxidation.

4.2. In plant control and water use minimization

Stream segregation is the initial step in implementing in-plant controls. Due to the difference in wastewater characteristics from beamhouse (high pH and sulfides), tanning and retanning (low pH and chromium) operations, more efficient control could be achieved through the use of a treatment process specifically designed for the related pollutant. Furthermore the segregation could lead to the reuse or recycling of spent liquors and the recovery of materials (Cassano et al., 2001). This is also foreseen by the legislative issues that within the EU, industrial emissions are regulated via the Integrated Pollution and Prevention Control Directive (IPPC) (96/61/EC, 1996; 2008/1/EC, 2008) of which the requirements of the IPPC had to be implemented into the law of the member states.

4.3. Greening production

Benzene- and naphthalene sulfonates are widely applied in tanning of hides and sulfo derivatives of naphthalene are observed in tannery wastewater at concentrations of 0.1–30 mgL^{-1} (Song et al., 2003). Naphthalenesulfonates and their substituted analogs have been reported to be poorly degradable (Stolz, 1999) which was correlated with either their molecular structure or their direct toxicity to potential microbial degraders (Ruff et al., 1999). The sulfonated compounds in wastewater are known to be degraded by several bacterial consortia but most of the xenobiotic organosulfonates are subject to desulfonation (Song and Burns, 2005).

Many researchers have attempted to improve cleaner chrome tanning processing (Suresh et al., 2001) or using alternative chemicals such as enzymes (Kanth et al., 2009), amino acids (Krishnamoorthy et al., 2012), oxazolidine (Sundarapandiyan et al., 2011). Further alternatives in dehairing process for waste minimization have come to agenda (Thanikaivelan et al., 2003; Valeika et al., 2009; Dettmer et al., 2013). Ultrasound has been exercised as an alternative technology to decrease chemicals use and leather quality (Sivakumar et al., 2009).

Chemical modification of chromium tanning salt is one of the options for enhancing the uptake of chromium. Synthetic tanning material based on chromium improved significantly (90%) chromium uptake. Chromium was complexed using multifunctional polymeric matrix. It was reported by Gupta and Babu (2009) that the chromium uptake using the chromium syntan was 90%. Sundarapandiyan et al. (2011) observed an enhancement of chromium uptake in tanning using oxazolidine and a decreasing of the chromium load in wastewater. Modification of process such as reduction of float is another tool for improving the chromium uptake (Morera et al., 2006). Carrying out chrome tanning without float and increasing the temperature at the end of the tanning process brought about 91% reduction in chromium discharged.

According to Bacardit et al. (2008), by reducing the float, the driving force for penetration is enhanced. The increase of the temperature to 55 °C also facilitated chromium uptake. The chromium emission was reported as 0.013 against 6.5 kg of Cr_2O_3 per ton of hide for traditional process.

Recently Manfred et al. (2012) has proposed CO_2 as process additive for free of water tanning. The replacement of ammonium salts in the deliming processes by carbon dioxide and the reuse of wastewater and chemicals after membrane filtration of the deliming/bating liquor was successfully proved by Gallego-Molina et al. (2013). The implementation of both measures resulted in 53% total nitrogen reduction when compared with deliming using ammonium salts and not reusing. Moreover deliming baths using CO_2 showed a similar efficiency in the process of calcium removal from the hide.

5. Conclusion

The present work highlighted the current and future pollution prevention measures in leather tannery. It has been well established that chemical coagulation flocculation as a first treatment step is required to remove particulate material and other pollutants as well as chromium VI which inhibits biological treatment.

Basically to apply segregation of waste streams approach in tannery pollution prevention is the most important step although it is not widely and practically applied in the world. Organization of tanneries in the industrial districts is another common approach which helps much to abate the pollution in parallel to the strengthening discharge limits. However integrated pollution prevention strategy of the EU and the greening economy which includes the shifting chemicals with the natural ones, water minimization technologies and water recycling this sector will continue to spend efforts for solving environmental problems. This paper revising all above mentioned issues with the particular focus on the emerging technologies to control xenobiotics in the tanners effluents and with the possible reuse of treated wastewater or segregated streams in the industry. It appears that emerging technologies are promising to remove xenobiotics however they still need to be optimized for economics. It is not yet possible to distinct which process is the best solution among few data sets found in the literature, however it is clear that continuous efforts would gain more audience to increase these data sets in the near future.

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