

Environmental Pollution, Toxicity Profile and Treatment Approaches for Tannery Wastewater and Its Chemical Pollutants

Gaurav Saxena, Ram Chandra, and Ram Naresh Bharagava

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G. Saxena • R.N. Bharagava (✉)

Laboratory for Bioremediation and Metagenomic Research (LBMR),
Department of Environmental Microbiology (DEM), School for Environmental Sciences (SES),
Babasaheb Bhimrao Ambedkar University (A Central University),
Vidya Vihar, Raebareli Road, Lucknow 226 025, Uttar Pradesh, India
e-mail: bharagavarnbbau11@gmail.com; ramnaresh_dem@bbau.ac.in

R. Chandra

Environmental Microbiology Section, Environmental Toxicology Group, Council of Scientific
and Industrial Research (CSIR), Indian Institute of Toxicology Research (IITR),
Post Box 80, M.G. Marg, Lucknow 226 001, Uttar Pradesh, India

1 Introduction

Leather industries (LIs) play an important role in the national economy of many developing countries like India, China, Turkey, Brazil, Ethiopia, Pakistan and Bangladesh (Leta et al. 2004; Lefebvre et al. 2006; Kurt et al. 2007; Verma et al. 2008; Haydar and Aziz 2009; Lofrano et al. 2013; Chowdhury et al. 2013; Wang et al. 2014). Approximately, 22,700.5 M ft² (or 2108.94 M m²) of leather is produced annually in the world (FAO 2008) and the world trade for the leather sector is estimated as US\$100 billion per year (UNIDO 2010). The demand for leather and leather products is ever increasing and independent of supply. The United States, Germany and other European countries are the major importers whereas the countries like India, China, Pakistan, Egypt, Brazil, Thailand and Indonesia are the major exporters of leather and leather products.

Unfortunately, LIs are also one of the major polluters worldwide because of the complex nature of their wastewaters. During leather production, a variety of chemicals with large volumes of water are used to convert the raw hide/skins into leather or leather products generating large volumes of high strength wastewater, which are a major source of environmental pollution. The wastewater generated is characterized by a high chemical oxygen demand (COD), biological oxygen demand (BOD), Total dissolved solids (TDS), Total suspended solids (TSS), chromium (III) and phenolics with high pH, strong odor and dark brown color (Durai and Rajasimmam 2011; Suganthi et al. 2013; Dixit et al. 2015). Apart from high organic content, tannery wastewater (TWW) also contains various nutrients such as nitrogen and phosphorus that can lead to eutrophication of water bodies (Rai et al. 2005; Durai and Rajasimmam 2011; Raj et al. 2014). In addition, the dark brown color of wastewater hinders the photosynthesis process by blocking the sunlight penetration and it is therefore deleterious to aquatic life (Aravindhan et al. 2004; Rai et al. 2005; Kongjao et al. 2008; Mwinyihija 2010; Durai and Rajasimmam 2011). However, the major pollutants present in TWW include chromium, tannins or syntans (STs), phenolics, phthalates and azo dyes (Kumar et al. 2008; Lofrano et al. 2013; Dixit et al. 2015).

The high concentration and low biodegradability of pollutants present in TWW is a major cause of serious environmental concern (Di Iaconi et al. 2002; Schrank et al. 2009) and thus, it is imperative to adequately treat the TWW before its final disposal in the environment. However, the increasingly stringent environmental regulations are also forcing the LIs to improve the treatment processes applied at wastewater treatment plants (WWTPs) and also explore the alternative methods for the better treatment and management of TWW.

Therefore, this paper highlights the environmental impacts and toxicity profile of TWW and chemicals and provides a detailed review on the existing treatment approaches for its safe disposal into the environment. The emerging treatment approaches have been discussed with their merits and demerits. Further, the emerging anammox technology for the removal of ammonia from TWW and constructed wetlands (CWs) for wastewater treatment has been discussed. In addition, the clean

technologies (CTs) for waste minimization, control and management in LIs are discussed. Moreover, the international legislation scenario on discharge limits for TWW and chemicals has also been discussed country wise with discharge standards to prevent the environmental pollution.

2 Leather Production and Chemicals Used in Tanning Process

LIs are specialized in processing of hide (skins of large animals like cows, buffaloes and horses) and skins (skins of small animals like sheep, goats and calves) for leather production. The tanning process used to convert the hide/skins (a highly putrescible material) into stable and imputrescible products termed as leather, which is used for various purposes (Dixit et al. 2015). Tanning processes are classified into vegetable or chrome tanning depending on the type of tanning reagent (tannins or chromium) applied (Ram et al. 1999; Mannucci et al. 2010) (Table 1). The steps and overall process of leather production are well described in

Table 1 Comparison between vegetable tanning and chrome tanning process

S. No.	Parameters	Vegetable tanning	Chrome tanning
1.	Tanning agent	Vegetable tannins (VTs)	Chromium salt
2.	Nature	Organic tanning	Inorganic (mineral) tanning
3.	Action	Slow process	Fast process
4.	Cost	Costly affairs	Cost effective
5.	Time	Time consuming	Less time consuming
6.	Geographical use	Used in developed countries and few developing countries	Used in developing countries
7.	Products	Heavy leather like shoe soles, luggage, saddlery and belt etc.	Light weight leathers like shoe uppers, garments and bag etc.
8.	Product characteristics	Higher thermal stability and water resistant	Softer and more pliable leather
9.	Processing steps	All the steps are same as in chrome tanning process	Additionally, retanning, dyeing and fatliquoring are usually performed to produce finished leather and a preliminary degreasing step may be necessary when using animal skins, such as ship skins
10.	Environmental Impact	Does not require prior preparation of pickling and therefore contribution to pollution load from sulfate salts are lower hence ecofriendly, but VTs are hard to biodegrade. Thus, waste bearing VTs degrade slowly	Generation of chromium containing sludge and wastewater is still a major environmental problem of chrome tanning process

the literature (Thanikaivelan et al. 2005; ILTIP 2010; Lofrano et al. 2013; Dixit et al. 2015). However, the tanning process involves different steps and chemicals for different end products and the kind and amount of waste generated may vary in a wide range of quantity and nature (Lofrano et al. 2013).

During the tanning process, a large amount of chemicals such as acids, alkalis, chromium salts, tannins, sulfates, phenolics, surfactants, dyes, auxiliaries, sulphonated oils and biocide etc. are used to convert the semi-soluble protein “collagen” present in hide/skins into highly durable commercial forms of leather, and the chemicals used are not completely fixed by the hide/skins and end up in wastewater (Lofrano et al. 2008; Mannucci et al. 2010). The poor uptake of chromium salt (50–70 %) during the tanning process results in the material wastage on one hand and disturbance of the ecological balance on the other hand (Saravanbahavan et al. 2004; Dixit et al. 2015). Moreover, the sulfonated oils and synthetic tannins or syntans (STs) (an extended set of chemicals such as phenol, naphthalene, formaldehyde, melamine and acrylic resins) are also used in tanning/retanning process to make the leather more softer (Lofrano et al. 2008, 2013).

Many regulations have been passed to avoid the use of hazardous chemicals in industrial processes such as Integrated Pollution Prevention and Control Directive (96/61/EC 1996; 2008/1/EC 2008). The Directive (REACH) (EC 1907/2006) for European Regulatory Framework on chemicals namely Registration, Evaluation, Authorization and Restriction of Chemical substances directed the LIs to avoid the use of those leather auxiliaries and basic chemicals, which are not registered and listed in the Safety Data Sheet (Lofrano et al. 2013). Moreover, the Directive (2003/53/EC) restricted the marketing and use of products/product formulations containing >0.1 % of nonyl ethoxyphenol (NPE) or nonylphenol (NP) and their use in making of the leather products in Europe (Lofrano et al. 2008). In addition, the Directive (1999/815/EC) has directed the industries to label the products if they contain >0.5 % phthalates (benzyl butyl phthalate, di-butyl phthalate and di-ethyl hexyl phthalate) due to the reproductive toxic potential of the phthalates (EU 2003). The use of o-phenyl phenol is restricted for leather finishing due to its carcinogenic potential (EPA 2007) and the use of formaldehyde (a cross liker casein top coats) due to its carcinogenic potential has been also restricted (EU 1998). The inorganic compounds such as cadmium sulfate and lead chromate (fastening agents) are highly toxic in nature (IARC 2004; ATSDR 2008). Further, the EU Azo Colorants Directive (2002) has prioritized several azo dyes and restricted their use in LIs due to higher toxicity but there is no any particular restriction to use STs yet in LIs worldwide (Dixit et al. 2015).

3 Tannery Wastewater: Nature and Characteristics

Water is crucial for life and also used in many industrial processes. In the tanning process, a large quantity of water and chemicals are used to treat raw hide/skins and approximately 30–35 m³ of wastewater is generated per ton of raw hide/skins processed (Lofrano et al. 2008; Islam et al. 2014). However, the wastewater

generation depends on the nature of raw material, finishing product and production processes applied (Tunay et al. 1995; Lofrano et al. 2013). This presents two major problems for LIs: First, the availability of good quality of water and second is the adequate treatment of such a large volume of highly contaminated wastewater.

Tannery wastewater (TWW) is a basic, dark brown coloured waste having COD, BOD, TDS, chromium (III) and phenolics with high pH and strong odor (Durai and Rajasimmam 2011; Suganthi et al. 2013; Dixit et al. 2015). However, the characteristics of TWW may vary from industry to industry, raw materials and chemicals used, type of final product and the production processes adopted by LIs (Apaydin et al. 2009; Rameshraj and Suresh 2011; Lofrano et al. 2013).

During leather production, the beamhouse and tanning operation are the high pollution causing steps because beamhouse operation contributes high organic and sulfide content whereas tanning operation contributes high salts (of chloride, ammonium, chromium and sulfate) concentrations in TWW (Cooman et al. 2003; Rameshraj and Suresh 2011). Hence, the beamhouse wastewater is characterized by an alkaline pH and tanning wastewater by a very acidic pH as well as a high COD value (Lofrano et al. 2013). Generally, TWW is highly rich in nitrogen, especially organic nitrogen, but very poor in phosphorous (Durai and Rajasimmam 2011). The retanning streams relatively have a low BOD and TSS (Total suspended solids), but high COD and contain trivalent chromium (III), tannins, sulfonated oils and spent dyes whereas the wet finishing, retanning, dyeing and fat liquoring processes contribute low fractions of salt in TWW that is predominantly originating from the hide/skins in the soak liquor (USEPA 1986; Lofrano et al. 2013). Further, BOD₅/COD (due to inhibitors) or BOD₅/TOC (due to high sulfide and chloride concentration) ratio is used for the biodegradation study of TWW (Lofrano et al. 2013). The data on wastewater generation and pollution load of each step during the processing of raw hide/skins are presented in Table 2.

Table 2 Pollution load and quantity of wastewater generated during the processing of per ton raw hide/skins

Pollution load	Processing operation (load kg/ton of raw hide/skins)				Post-tanning	Finishing
	Soaking	Unhairing/liming	Deliming and bating	Chrome tanning		
Wastewater generated (m ³ or kL)	9.0–12.0	4.0–6.0	1.5–2.0	1.0–2.0	1.0–1.5	1.0–2.0
TSS	11–17	53–97	8–12	5–10	6–11	0–2
COD	22–33	79–122	13–20	7–11	24–40	0–5
BOD	7–11	28–45	5–9	2–4	8–15	0–2
Cr	–	–	–	2–5	1–2	–
Sulphides	–	3.9–8.7	0.1–0.3	–	–	–
NH ₃ -N	0.1–0.2	0.4–0.5	2.6–3.9	0.6–0.9	0.3–0.5	–
TKN	1–2	6–8	3–5	0.6–0.9	1–2	–
Chlorides	85–113	5–15	2–4	40–60	5–10	–
Sulfates	1–2	1–2	10–26	30–55	10–25	–

Adapted from Dixit et al. (2015)

4 Environmental Pollution and Toxicity Profile of Tannery Wastewater

TWW is ranked as one of the major environmental pollutants among all the industrial wastewaters (Verma et al. 2008; Gupta et al. 2012). The presence of a variety of toxic and hazardous chemicals such as chromium, chlorophenols, formaldehydes, STs, oils, resins, biocides, detergents and phthalates etc. in TWW creates a negative image of LIs (Lofrano et al. 2013; Dixit et al. 2015). The toxicity of chemicals used during leather processing is summarized in Table 3. The wastewater generated from Common Effluent Treatment Plant (CETP) contains high BOD, COD, TDS and a variety of toxic heavy metals especially chromium, which makes it potentially toxic for humans and other living beings (Mondal et al. 2012; Lofrano et al. 2013; Dixit et al. 2015). In addition, TWW also contains a mixture of chemical compounds, which are used during leather processing and are not get properly degraded even after the conventional treatment and have a negative impact on living organisms and environment (Alvarez-Bernal et al. 2006; Oral et al. 2007; Kumar et al. 2008; Tigini et al. 2011; Siqueira et al. 2011; Shakir et al. 2012; Lofrano et al. 2013; Saxena and Bharagava 2015).

Table 3 Applications, toxicity and LD₅₀ for chemicals used during leather production in leather industry (Adapted from Kumar et al. 2008; Dixit et al. 2015)

Name of chemicals	Applications	LD ₅₀ in rats (oral mg/kg)	Target organs
Pentachlorophenol (PCP) (a carcinogen)	Applied as a biocide in preservative for raw hides/skins	2000	Eyes, nose, skin, respiratory tract, blood, kidney, liver, immune system and reproductive system
Di-butyl phthalate (DBP) (a endocrine disrupting chemical)	Applied as a plasticizer in artificial leather manufacturing	7499	Eyes, lungs, gastrointestinal (GI) tract and testes
Benzyl butyl phthalate (BBP) (a endocrine disrupting chemical)	Applied in preparation of micro-porous artificial leather coating/water vapour-permeable sheet materials	2330	Eyes, lungs, liver and reproductive system
Bis(2-ethylhexyl) phthalate (DEHP) (a endocrine disrupting chemical)	Applied as a plasticizer in artificial leather manufacturing	30,000	Liver and testes
Short chain, chlorinated paraffin's	Additive for leather treatment (gives smoothness), leather clothing and belts and as oiling agent	3090	Liver, kidney and thyroid

(continued)

Table 3 (continued)

Name of chemicals	Applications	LD ₅₀ in rats (oral mg/kg)	Target organs
Anthracene (a carcinogen)	Additive during tanning	16,000	Kidneys and liver
Nonyl phenol (a endocrine disrupting chemical and xenoestrogen)	Applied during finishing	1475	Blood. Lungs, eyes, skin, central nervous system (CNS), kidneys and testes
N-methyl pyrrolidone	Applied as a coalescence, plasticizers and wetting agents	3914	Eyes, kidneys, lymphatic system, liver, lung and testes
Methyl isothiazolinone (a carcinogen)	Applied as biocide	1800	Skin and eyes
Organotin compounds (Dibutyl tin) (a carcinogen)	Applied as a catalyst	175	GI tract and liver
Azo dyes (Orange II) (a carcinogen)	Applied as a dyeing agent	3418	Blood, liver and testes
Hexachlorobenzene (a carcinogen)	Applied for raw hide/skins preservation	10,000	Reproductive system
Chromium (a carcinogen)	Applied as a tanning agent	3250	Kidneys, CNS and hemato-poietic system
Formaldehyde (a carcinogen)	Applied in finishing of leather	100	Eyes and lungs
Arsenic (a carcinogen)	Applied in finishing of leather	763	Liver, kidneys, skin, lungs and lymphatic system
Sodium dichromate	Applied in preparation of chrome-tanning salts	NA	Blood, kidneys, heart, lungs and eyes
Cobalt dichloride	Applied in dyeing and finishing	80	Skin, lungs, liver, kidney and heart
Cadmium sulfate (Pigment)	Applied as fastening agents and used in marking and surfacing of material.	280	Lungs, liver, tissues and reproductive system
Lead chromate (pigment)	Applied as fastening agents and used in marking and surfacing of material.	1000	Lungs, liver, tissues and reproductive system

NA not available

TWW is a major source of water and soil pollution. The dark brown color blocks the sunlight penetration, and thus, reduces the photosynthetic activity and oxygenation of receiving water bodies and hence, becomes detrimental to aquatic life (Song et al. 2000; Kongjao et al. 2008; Bakare et al. 2009; Mwinyihija 2010; Carpenter et al. 2013). In addition, the depletion in dissolved oxygen encourages the anaerobic condition, which leads to the putrefying odour of receiving water bodies (Rai et al. 2005; Sahu et al. 2007; Verma et al. 2008). TWW also causes

eutrophication of polluted water bodies and thus adversely affecting the ecological functioning of aquatic resources (Rai et al. 2005; Durai and Rajasimmam 2011; Schilling et al. 2012; Dixit et al. 2015). The high concentration of heavy metals in sediments of the Ganga river and its tributaries has been reported (Singh et al. 2003; Tare et al. 2003; Bhatnagar et al. 2013). The increase in the salinisation of rivers and groundwater has led to the reduction in soil fertility and quality of drinking water in Tamil Nadu, India (Money 2008). It has been estimated that over 55,000 ha of land has been contaminated by TWW and around five million peoples are affected by low quality of drinking water and social environment (CSIRO 2001; Sahasranaman and Jackson 2005). TWW is also reported to inhibit the nitrification process (Szpyrkowicz et al. 2001; Trujillo-Tapia et al. 2008; Lofrano et al. 2013) as well as to cause a huge foaming problem on surface waters (Schilling et al. 2012).

Moreover, the treated/partially treated TWW causes severe toxic effects in fishes and other aquatic organisms. The genotoxicity and mutagenicity of water polluted with TWW has been evaluated by the micronucleus test and the comet assay by using fish *Oreochromis niloticus* (Matsumoto et al. 2006). De Nicola et al. (2007) have studied the toxicity of mimosa tannin and phenol-based syntans on sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) during the early developmental stages and on marine algal cell growth (*Dunaliella tertiolecta*) and reported the sea urchin embryogenesis was affected by vegetable tannins and syntan water extracts at a level of 1 mg L^{-1} . Afaq and Rana (2009) also studied the impact of leather dyes (Bismarck brown and acid leather brown) on the protein metabolism in fresh water teleost, *Cirrhinus mrigala* (Ham.) and reported a significant decrease in total protein content in teleost treated with leather dyes. In addition, the toxic effects of TWW on the survival and histopathological parameters in the different organs of fishes *Channa punctatus* and *Oreochromis mossambicus* have been studied (Mohanta et al. 2010; Navaraj and Yasmin 2012). However, the toxic effects of TWW on the hematological parameters of a common fish *Tilapia mossambica* and fresh water fish, *Labeo rohita* (Hamilton) has also been recently studied (Lesley Sounderraj et al. 2012; Praveena et al. 2013). Further, TWW was also reported to interfere with the metabolic processes by altering the activity of oxidative enzymes in different organs of guppy fish, *Poecilia reticulata* and thereby causing cellular injury as a result of exposure (Aich et al. 2011, 2015).

Further, the presence of pathogens in water and wastewater has been reviewed by many workers (Bharagava et al. 2014; Saxena et al. 2015). TWW are also highly rich in organic and inorganic constituents and thus, may provide a chance to a variety of pathogenic bacteria to flourish and contaminate the receiving water bodies as these constituents may act as a source of nutrients (Verma et al. 2008; Bharagava et al. 2014). Recently, Chandra et al. (2011) have reported the presence of various types of organic pollutants (OPs) and bacterial communities in two aeration lagoons of a CETP used for the degradation and detoxification of TWW in India and also tested the toxicity of TWW on mung bean (*Phaseolus mungo*) in terms of seed germination and seedling growth. In addition, various authors have also assessed the bacteriological quality of TWW and reported the presence of a variety of pathogenic bacteria remained in TWW even after the secondary treatment process (Verma et al. 2008; Ramteke et al. 2010; Bharagava et al. 2014).

Generally, LIs discharges their wastewater into nearby canals/river, which are directly/indirectly being used by farmers for the irrigation of agricultural crops (Trujillo-Tapia et al. 2008; Gupta et al. 2012). This practice leads to the movement of potentially toxic metals like chromium from water to crop plants that ultimately reach into the human/animal body and cause toxicity (Sinha et al. 2008; Chandra et al. 2009). However, the chromium toxicity mainly depends on the chemical speciation and thus, the associated health effects are influenced by the chemical forms of exposure (Rameshraj and Suresh 2011). It is well reported that chromium (VI) is a potent carcinogen for humans, animals, plants as well as microbes as it enters the cells *via* surface transport system and get reduced into chromium (III) form and causes various genotoxic effects (Ackerley et al. 2004; Aravindhan et al. 2004; Matsumoto et al. 2006; Tripathi et al. 2011; Raj et al. 2014). Thus, the use of Cr loaded TWW for the irrigation of agricultural crops disrupts the several physiological and cytological processes in cells (Shanker et al. 2005; Chidambaram et al. 2009; Gupta et al. 2012) leading to the reduction in root and shoot growth and biomass, seed germination, seedling growth (Lopez-Luna et al. 2009; Hussain et al. 2010), and also induces the chlorosis, photosynthetic impairment and finally leading to the plant death (Akinici and Akinici 2010; Asfaw et al. 2012). However, the effect of TWW on seed germination and seedling growth is governed by its concentration and it is crop-specific. In a recent study conducted on mung bean (*Vigna radiate* (L.) wilczek) by Raj et al. (2014), the percent inhibition of seed germination was 90 % and 75 %, when seeds were treated with 25 % untreated and treated TWW, respectively. Moreover, it is also reported that treated and adequately diluted TWW can be used for the irrigation of agricultural crops as it provides a reliable source of water supply to farmers and contains valuable plant nutrients especially N, P, K and also add organic matter to soil (Trujillo-Tapia et al. 2008; Durai and Rajasimmam 2011; Asfaw et al. 2012; Sangeetha et al. 2012; Kohli and Malaviya 2013). Further, the genotoxic and mutagenic effects of TWW and agricultural soil irrigated with TWW has been recently studied (Alam et al. 2009, 2010).

In addition, the inappropriate discharge of TWW also leads to significant levels of soil pollution as well as acidification because of high salt loads in wastewater (Chowdhury et al. 2004; Alvarez-Bernal et al. 2006; Mwinyihija 2010; Raj et al. 2014). High sulfide content in TWW also causes the deficiency of some micronutrients in soil such as Zn, Cu and Fe etc. (Raj et al. 2014). However, Cr (VI) alters the structure of soil microbial communities and reduces their growth and finally retards the bioremediation process and if it enters into the food chain, causes skin irritation, eardrum perforation, nasal irritation, ulceration and lung carcinoma in humans as well as animals along with accumulation in placenta impairing the fetal development in mammals (Cheung and Gu 2007; Chandra et al. 2011; Asfaw et al. 2012). In addition, the exposure to chlorinated phenols is possible particularly to pentachlorophenol (PCP), which is highly carcinogenic, teratogenic and mutagenic in nature and causes toxicity to living beings by inhibiting the oxidative phosphorylation, inactivating the respiratory enzymes and damaging the mitochondrial structure (Jain et al. 2005; Verma and Maurya 2013; Tripathi et al. 2011).

The high concentration of PCP can also cause the obstruction in circulatory system of lungs, heart failure and damage to central nervous system (USDHHS 2001; Tewari et al. 2011; Dixit et al. 2015).

In addition, TWW also contain azo dyes that are highly persistent in nature due to their complex chemical structure and xenobiotic nature leading to the environmental pollution (Nachiyar and Rajkumar 2003; Gurulakshmi et al. 2008; Mahmood et al. 2013; Baccar et al. 2011; Patel et al. 2012; Preethi et al. 2013; Dixit et al. 2015). Thus, the removal of azo dyes from TWW is essential because of their high mutagenicity, carcinogenicity and intense coloration problems of contaminated aquatic resources (Osugi et al. 2009; Saratale et al. 2010). The discharge of azo dyes into the surface water also leads to the aesthetic problems and obstruct the light penetration and oxygen transport into the water bodies and finally affecting the aquatic life (Khalid et al. 2008; Chen et al. 2011). Moreover, these dyestuffs have been also reported to cause some other serious problems such as dermatitis, skin and eye irritation and respiratory problems in human beings (Keharia and Madamwar 2003).

Further, there has been an increasing concern regarding the release of many endocrine disrupting compounds (EDCs) along with TWW in environment. EDCs disturb the delicate hormonal balance and compromise the reproductive fitness of living beings and ultimately may lead to carcinogenesis (Dixit et al. 2015). Kumar et al. (2008) have detected many EDCs like nonylphenol (NP), 4-aminobiphenyl, hexachlorobenzene and benzidine in TWW collected from the northern region of India and tested their toxicity on the reproductive system of male rats. However, the presence of phthalates (EDCs) such as bis(2-ethylhexyl)phthalate (DEHP), dibutyl phthalate (DBP), bis(2-methoxyethyl)phthalate in TWW has been also reported (Alam et al. 2009, 2010). Therefore, the adequate treatment of TWW prior to its final disposal into the environment is required.

5 Treatment Approaches for Tannery Wastewater and Chemicals

TWW is a major source of soil and water pollution and it is therefore essential to adequately treat the TWW prior to its safe disposal into the environment. This can be achieved by using physical, chemical and biological methods either alone or in combination.

5.1 Physico-Chemical Treatment Approaches

5.1.1 Coagulation/Flocculation

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive charge to reduce the negative

charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs) whereas flocculation is the action of polymers to form bridges between the flocs, and bind the particles to form large agglomerates or clumps. There are a number of coagulants such as aluminium sulfate (AlSO_4), ferric chloride (FeCl_3), ferrous sulfate (FeSO_4) etc. that are used to reduce the organic load (COD) and suspended solids (SS) as well as to remove toxic metals mainly chromium from TWW (Lofrano et al. 2013).

However, coagulants are pH specific and their effectiveness largely depends on their type and concentration and characteristics of the wastewater to be treated (Song et al. 2004). Ates et al. (1997) reported $>70\%$ removal of COD and $<5\text{ mg L}^{-1}$ of total chromium from TWW using alum and FeCl_3 based-CF. Song et al. (2004) also reported 30–37 % removal of total COD, 74–99 % of chromium and 38–46 % of SS by using 800 mg L^{-1} of alum at pH 7.5 from TWW containing 260 mg L^{-1} of suspended solids, 16.8 mg L^{-1} of chromium, 3300 mg L^{-1} of COD at pH 9.2 and finally concluded that FeCl_3 based CF proved better results than alum based-CF. Chowdhury et al. (2013) have reported 92 % removal of COD and 96 % of chromium from TWW using FeCl_3 at the concentration of 150 mg L^{-1} at pH 7 followed by sand-stone filtration process. In addition, Shegani (2014) also reported 81.60 %, 98.34 %, 92 %, 75.00 %, 70.00 %, 69.20 % and 50 % removal of COD, ammonia, nitrate, hexavalent chromium, phosphate, chloride and H_2S , respectively by using coagulants $\text{Ca}(\text{OH})_2$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, but a low reduction in sulfate (19.00 %) and TSS (13.00 %) and an increase in TDS (15.60 %) were observed.

Moreover, some coagulants such as poly-aluminium chloride (PAC), poly-aluminium silicate (PASiC) and poly-aluminium ferric chloride (PAFC) ($[\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}]_m. [\text{Fe}_2(\text{OH})_n\text{Cl}_{6-n}]_m$) have been developed with improved coagulation efficiency to minimize the residual coagulants in treated wastewater (Gao et al. 2004; Lofrano et al. 2013). Lofrano et al. (2006) reported $>75\%$ removal of COD and $>95\%$ of TSS from TWW at all doses of alum ($800\text{--}900\text{--}1000\text{--}1200\text{ mg L}^{-1}$) using PAFC (900 mg L^{-1}) at pH 8.5. Yoganand and Umapathy (in press) have also applied a green methodology for the recovery of chromium (VI) from TWW using newly synthesized quaternary ammonium salt and reported 99.99 % removal of chromium (VI) from TWW.

5.1.2 Adsorption

Adsorption is typically used for the removal of toxic metals especially chromium from TWW. There are a number of studies available on the use of adsorbents such as bentonite clay, cement kiln dust, activated carbon etc. for the treatment of TWW (Fadali et al. 2004; Fahim et al. 2006; Tahir and Naseem 2007). Further, the use of chitin-humic acid based hybrid and ground shrimp shells as adsorbent for the significant removal of Cr(III) from TWW has been reported (Santosa et al. 2008; Fabbicino et al. 2013). Moreover, the use of lime/bitten based coagulants and activated carbon as a post treatment of TWW is also suggested (Ayoub et al. 2011).

5.2 *Biological Treatment Approaches*

Biological approaches are the eco-friendly methods for the treatment of industrial wastewaters and involve the stabilization of waste by decomposing them into harmless inorganic solids either by aerobic or anaerobic processes. The most commonly used processes for the biological treatment of TWW are the Activated sludge process (ASP) and Upflow Anaerobic Sludge Blanket (UASB) process (Durai and Rajasimmam 2011).

5.2.1 *Aerobic Treatment*

In an aerobic treatment process, the waste decomposition rate is fast and also not characterized by unpleasant odours but a large amount of sludge is generated. There are several studies on the aerobic treatment of TWW using ASP as has been reported earlier by many workers (Jawahar et al. 1998; Eckenfelder 2002; Tare et al. 2003; Vidal et al. 2004; Hayder et al. 2007; Ramteke et al. 2010) and some of the important findings are summarized in Table 4.

TWW is highly saline in nature due to high load of salts, which are used for the preservation of raw hides/skins (Sundarapandiyan et al. 2010) and therefore, causes some serious problems in the biological treatment of TWW. The major problems include (Sivaprakasam et al. 2008): (a) limited adaptation of conventional cultures due to higher salt concentration ($>3\text{--}5\%$ w/v), that therefore could not effectively treat TWW (b) salt adaptation of cultures is easily lost when subjected to salt free medium, and (c) changes in the ionic strength (salt concentration from 0.5 to 2 % w/v) cause cell disruption even with the acclimatized cultures and finally lead to system failure.

However, the high concentration of poorly biodegradable compounds such as tannins and other toxic metals inhibit the biological treatment processes (Schränk et al. 2004). Cr (VI) is reported to inhibit the growth of heterotrophs as well as nitrifying/denitrifying bacteria (Stasinakis et al. 2002; Farabegoli et al. 2004). To overcome this problem, a Sequencing Batch Reactor (SBR) is highly efficient to carry out the biological treatment and nitrogen removal from TWW in the presence of inhibitors due to its low cost, flexible operation and selection and enrichment of a particular microbial species (Farabegoli et al. 2004; Ganesh et al. 2006; Murat et al. 2006; Durai and Rajasimmam 2011; Rameshraj and Suresh 2011; Faouzi et al. 2013; Lofrano et al. 2013).

Moreover, the fluctuation in temperature range also has adverse effects on the nitrification process. The fluctuation in the temperature range significantly affects the removal of organic carbon and nitrogen from TWW whereas it has a minor influence on COD removal efficiency (4–5 %) that has been studied for a full-scale activated sludge process based treatment plant used for TWW (Gorgun et al. 2007). Further, the improvement in the performance of the nitrification process through increased aeration and total nitrogen removal efficiency (up to 60 %) at a temperature range between 21 and 35 °C during an intermittent aeration type of operation has been reported (Insel et al. 2009).

Table 4 Microorganisms reported in the degradation of tannery wastewater

References	Microorganisms	COD removal (%)	BOD removal (%)	Cr removal (%)
Kim et al. (2014)	<i>Brachymonas denitrificans</i>	98.3	–	88.5
Noorjahan (2014)	<i>E. coli</i>	90	90	63.8
	<i>Bacillus</i> sp.	95.4	95.4	73.5
Elmagd and Mahmoud (2014)	Mixed culture	98.3	98.4	98.3
Sharma and Malaviya (2013)	<i>Fusarium chlamydosporium</i> SPFS2-g	71.80	–	–
Yusuf et al. (2013)	<i>B. subtilis</i>	87.6	–	–
	<i>P. fragi</i>	85.2		
El-Bestawy et al. (2013)	<i>Providencia vermicola</i> W9B-11, <i>Escherichia coli</i> O7:K1 CE10, <i>Bacillus</i> sp. 58, <i>Bacillus amyloliquefaciens</i> T004, <i>Pseudomonas stutzeri</i> M15-10-3, <i>Bacillus</i> sp. PL47	79.16	94.14	93.66
Mandal et al. (2010)	<i>Thiobacillus ferrooxidans</i>	69	72	5
Nanda et al. (2010)	<i>Nostoc</i> sp.	37.8	48.6	–
Ramteke et al. (2010)	<i>E. coli</i>	98.46	90	–
	<i>Vibrio</i> sp.	87.5		
	<i>Pseudomonas</i> sp.	96.15		
Sivaprakasam et al. (2008)	<i>P. aeruginosa</i> , <i>B. flexus</i> , <i>E. homiense</i> , <i>S. aureus</i>	80	–	–
Vankar and Bajpai (2008)	<i>Trichoderma</i> sp.	–	–	97.93
Onyancha et al. (2008)	<i>S. condensate</i>	–	–	>75
	<i>R. hieroglyphicum</i>			
Srivastava et al. (2007)	<i>Acinetobacter</i> sp.	–	–	90
Rajasimman et al. (2007)	Mixed culture	46–85	65–93	–
Wang et al. (2007)	<i>A. Thiooxidans</i>	–	–	99.7
Srivastava and Thakur (2006)	<i>Aspergillus</i> sp.	–	–	–
	<i>Hirsutella</i> sp.			70
Lefebvre et al. (2005)	Halophiles	95	–	–
Thanigavel (2004)	Mixed culture	89.5	–	–
Shakoori et al. (2000)	Bacterial strain	–	–	87

5.2.2 Anaerobic Treatment

The use of anaerobic treatment processes to treat TWW is an interesting option as compared to aerobic treatment process because of low energy consumption and sludge production. However, its full scale application has several drawbacks (Mannucci et al. 2010): i) continuous production of sulfide (from sulfate reduction) in absence of alternative electron acceptors such as oxygen and nitrate; ii) high protein content affects the selection of biomass, slow down the kinetics of hydrolysis and also inhibit the sludge formation, and iii) requirement of an additional aerobic treatment to meet the high COD removal.

The sulfide mainly inhibits the methanogenesis process during the anaerobic treatment of TWW and this might be due to the direct toxicity of sulfide, substrate competition between the sulfate reducing bacteria and methanogenic bacteria and precipitation of trace elements (Midha and Dey 2008; Rameshraj and Suresh 2011; Mannucci et al. 2014). However, the mechanisms of sulfide toxicity are not well understood.

The anaerobic treatment of TWW is mainly performed by using either the anaerobic filters (AF) composed of both upflow anaerobic filters (UAF) and down-flow anaerobic filters (DAF) or Upflow Anaerobic Sludge Blanket (UASB) reactors (Lefebvre et al. 2006; Rajasimman et al. 2007; El-Sheikh et al. 2011; Dixit et al. 2015). Beside these, the use of expanded granular sludge bed (EGSB) and anaerobic baffled reactor (ABR) for the treatment of TWW is also suggested (Zupancic and Jemec 2010).

In addition, the anaerobic treatment of TWW is more favorable in tropical countries having higher temperatures such as India, Pakistan, China, and Brazil etc. as compared to European countries (Durai and Rajasimman 2011; Mannucci et al. 2014). In these countries, the spread of new and large industrial areas to establish the LIs favor the development of centralized WWTPs. However, the application of anaerobic treatment processes at large scale makes it possible to balance the high operation and management costs with energy saving over the traditional aerobic treatment processes.

5.2.3 Constructed Wetlands and Treatment Ponds

Constructed wetlands (CWs) are man-engineered, eco-friendly systems designed to remove the pollutants from highly polluted industrial and municipal wastewaters. The use of CWs for the treatment of industrial wastewater has developed rapidly in current years and is now successfully employed to remove a diverse array of pollutants from wastewaters.

The proper functioning of a wetland system depends on the complex relationship between the plants, microorganisms, soil, wastewater characteristics and operational parameters (Aguilar et al. 2008). In this regard, several efforts have been made to select the suitable plant species capable to tolerate and remove the

pollutants from TWW (Mant et al. 2004; Calheiros et al. 2007, 2008, 2012), selecting the suitable supporting media/substrate for proper growth and development of wetland plants (Calheiros et al. 2008), as well as to study the bacterial community dynamics in CWs (Aguilar et al. 2008; Calheiros et al. 2009a, b). The plant roots and rhizomes are the major sites of microbial degradation/transformation of pollutants and subsequently the purification of wastewater because microbes form a biofilm on root surface and substrates (Stottmeister et al. 2003; Gagnon et al. 2007; Munch et al. 2007). However, the availability of nutrients or other environmental parameters affects the biofilm formation (Kierek-Pearson and Karatan 2005). Therefore, the detailed profiling of complex microbial populations is required to understand the proper functioning of CWs and phytoremediation processes (Chandra et al. 2015). Culture-dependent techniques are known to be insufficient to study the microbial community structure because numerous microorganisms are unculturable in lab conditions (Ward et al. 1990). Hence, molecular techniques such as random amplified polymorphic DNA (RAPD), polymerase chain reaction (PCR) and denaturation gradient gel electrophoresis (DGGE), is used for the study of microbial community structure, composition and diversity in CW system (Calheiros et al. 2009a, 2012).

Mant et al. (2004) have studied the phytoremediation potential of *Penisetum purpureum*, *Brachiaria decumbens* and *Phragmites australis* in CWs for the removal of chromium (ranging from 10 and 20 mg Cr dm⁻³) from TWW. In addition, the potentials of *Canna indica*, *Typha latifolia*, *P. australis*, *Stenotaphrum secundatum* and *Iris pseudacorus* in CWs for the treatment of TWW under two different hydraulic loading rates at 3 and 6 cm/day has been studied and it was found that only *P. australis* and *T. latifolia* were able to establish successfully (Calheiros et al. 2007). Further, these authors also evaluated *Arundo donax* and *Sarcocornia fruticosa* in two series of horizontal subsurface flow CWs used to treat TWW received from a conventional biological treatment plant and reported the removal of COD (51 and 80 %) and BOD₅ (53 and 90 %) for COD inlet: 68–425 mg L⁻¹ and for BOD₅ inlet: 16–220 mg L⁻¹ (Calheiros et al. 2012). In addition, the use of TWW as a growth medium for *Arthrospira* (*Spirulina*) has been recently suggested (Dunn et al. 2013). However, the chromium salt can be retained in wetlands with non-specialized supporting media (Dotro et al. 2012).

On the other hand, the use of treatment ponds for the treatment of TWW can also be an effective approach. The effect of different environmental parameters like pH, temperature and dissolved oxygen on the efficiency of a pilot-scale advanced integrated wastewater treatment pond system (AIWTPSs) used to treat TWW has been reported by Tadesse et al. (2004). They also suggested a combination of advanced facultative pond (AFP), secondary facultative pond (SFP) and maturation pond (MP) in a series for the effective treatment of TWW. Recently, Kumar and Sahu (2013) have designed the anaerobic pond (AP) for the treatment of TWW in Egypt.

5.3 *Emerging Treatment Approaches*

The TWW discharged even after the conventional treatment process still contains many refractory and recalcitrant organic pollutants (ROPs) and thus, require further treatment for environmental safety. Therefore, in order to overcome this problem, the use of emerging treatment technologies is increasing in recent years.

5.3.1 **Membrane Technologies**

Membrane technologies (MTs) are used for the mechanical separation/purification of industrial wastewater with the help of permeable membranes. MTs operate without heating and therefore use less energy than conventional thermal separation processes such as distillation, sublimation or crystallization. The use of MTs in LIs is becoming popular in current years because of continually reducing cost and ever extending application possibilities.

The MTs offer many economic benefits to the LI, especially the recovery of chromium from TWW (Lawanda et al. 2009; Ranganathan and Kabadgi 2011) and are used for purification/reuse of wastewater and chemicals of deliming/bating liquor (Gallego-Molina et al. 2013), reduction of pollution load due to unhairing and degreasing (De Pinho 2009; Wang et al. 2011), removal of salts as well as in the biological treatment of TWW for its reuse (Lofrano et al. 2013). Several membrane-based technologies such as cross flow microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and supported liquid membranes (SLMs) can be used for the removal of pollutants from TWW (Lofrano et al. 2013; Dixit et al. 2015). However, the use of reverse osmosis (RO) with a plane membrane has been suggested as a post treatment for the removal of refractory compounds such as chlorides and sulfates, and resulted in the production of high quality of permeate that allowed the reuse of tannery wastewater within the production cycle and thus, reduced the groundwater consumption (De Gisi et al. 2009). The economical evaluation of membrane filtration technologies has been discussed in detail by Scholz and Lucas (2003). The successful integration of MTs in a conventional purification process for TWW streams has been recently reported by Stoller et al. (2013).

5.3.2 **Membrane Bioreactors**

A membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and is now widely used for municipal and industrial wastewater treatment. MBRs offer several advantages over the conventional activated sludge treatment process (CASTP) such as elimination of sludge from settling basins, independence of process performance from filamentous bulking or other phenomena that affect the sludge settleability

(Munz et al. 2008; Suganthi et al. 2013; Dixit et al. 2015). The presence of tannins in TWW reduces the kinetics of nitrification without large differences between the biomass selected with either the CASTP or the MBR used (Munz et al. 2009). However, the major drawbacks of membrane application are the significant fouling due to clogging, adsorption and formation of cake layer by pollutants like residual organics, dyes, and other impurities onto the membrane (Srinivasan et al. 2012; Stoller et al. 2013). However, the extensive work is in progress to reduce the bio-fouling problem in MBRs. Further, a hybrid membrane bioreactor (HMBR), which is the integration of various treatment technologies, may be a solution to overcome the bio-fouling problem of MBRs. More recently, the efficiency of HMBR (activated sludge process + electro-coagulation) for the effective removal of COD and color from TWW satisfying the discharge limits set by Tamil Nadu Pollution Control Board (TPCB) India has been evaluated (Suganthi et al. 2013).

5.3.3 Anammox Technology

The anammox technology is used for the anaerobic removal of ammonia from TWW and it is currently emerging because of its low cost and energy consuming nature (Anjali and Sabumon 2014). It involves the anoxic oxidation of ammonia with nitrite as a preferred electron acceptor and consumes 50 % less oxygen, 100 % less organic carbon and saves 90 % of operational costs in sludge disposal as compared to the conventional nitrification/denitrification processes (Anjali and Sabumon 2014). Therefore, industries, producing wastewaters having a high concentration of ammonia, are showing increased interest in the anammox process. However, the long start-up time and inhibitive nature in the presence of organic carbon and $\text{NH}_4\text{-N}$ limits its field applications. Therefore, it is imperative to develop the mixed consortium capable of anammox in the presence of organic compounds. Further, the development of mixed microbial consortium consisting of ammonia oxidizing bacteria, anammox bacteria, and denitrifying bacteria is also expected to treat the wastewaters containing both ammonia and organic carbon.

5.3.4 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) refers to the set of chemical treatment processes that use strong oxidizing agents (O_3 , H_2O_2) and/or catalysts (Fe, Mn, TiO_2) and sometimes also use the high-energy radiation, e.g., UV light (Schrack et al. 2004; Naumczyk and Rusiniak 2005; Srinivasan et al. 2012; Dixit et al. 2015). AOPs are based on the production and utilization of hydroxyl radicals, which are strong oxidizing agents and quickly and non-selectively oxidize a broad range of recalcitrant organic pollutants such as benzoquinone, benzene, phenols, chlorophenols, dyes and formaldehyde in less time (Lofrano et al. 2013; Dixit et al. 2015). Generally, the AOPs are used to treat the secondary treated wastewater and therefore known as tertiary treatment (Audenaert et al. 2011). In this, most of the pollutants get converted into

stable inorganic compounds such as H_2O , CO_2 and salts, i.e. they undergo mineralization (Rameshraj and Suresh 2011). The treatment efficiency of AOPs is mostly evaluated in terms of COD removal however, TOC is a more suitable parameter to study the state of mineralization (Schrang et al. 2004, 2005; Costa et al. 2008; Monteiro Paschoal et al. 2009). There are various types of AOPs such as fenton oxidation, photo-oxidation, photo-fenton oxidation, ozonation, photocatalysis and electrochemical treatment processes that are applied to treat the TWW (Rameshraj and Suresh 2011; Lofrano et al. 2013; Dixit et al. 2015). The overall goal of AOPs used for TWW treatment is to reduce the pollution load and toxicity to such an extent that the treated TWW may be reintroduced into the receiving water bodies or reused during the process. The important findings of various AOPs applied to treat the TWW are presented in Table 5.

Table 5 Findings of some advanced oxidation processes (AOPs) applied for the treatment of tannery wastewater

References	AOPs	Wastewater type	Influent COD ($mg\ L^{-1}$)	Operation parameters and reduction in pollutants
Modenes et al. (2012)	Photo-Fenton ($UV/Fe^{2+}/H_2O_2$)	Equalized tannery wastewater	11,878	COD removal (90 %), TSS removal (50 %), Fe^{2+} ($0.4\ g\ L^{-1}$) and H_2O_2 ($15\ g\ L^{-1}$), Irradiation time (540 min)
Houshyar et al. (2012)	Ozone	Pre-alkalized tannery wastewater	2177	COD removal (30–70 %), Time (120 min), Ozone flow rate ($1-8\ g/h$)
Di Iaconi et al. (2010)	Ozone	Biologically treated tannery wastewater	2900	COD removal (97 %), TSS removal (96 %), TKN removal (91 %), Surfactants removal (98 %), Color removal (96 %)
Sundarapandiyar et al. (2010)	Electrochemical treatment	Synthetic tannery wastewater	10,715	COD removal (89 %), pH 3–9, Current density ($0.006-0.024\ A\ cm^{-2}$), Time (120 min)
Preethi et al. (2009)	Ozone	Raw tannery wastewater	5000	COD removal (60 %), O_3 flow rate ($2 \times 10^{-3}\ m^3\ min^{-1}$), Time (20–120 min) and pH (4)
Espinoza-Quinones et al. (2009)	Electrochemical treatment	Equalized tannery wastewater	17,618	COD removal (51–56 %), TSS removal (30–70 %), Electric current flow rate (0–10 A at 0–30 V), Time (30–45 min)
Costa et al. (2008)	Electrochemical treatment	Equalized tannery wastewater	1005 (TOC)	Maximum phenol removal (83.9 %), Maximum TOC removal (40.5 %), Time (5 h of electrolysis)

(continued)

Table 5 (continued)

References	AOPs	Wastewater type	Influent COD (mg L ⁻¹)	Operation parameters and reduction in pollutants
Kurt et al. (2007)	Electrochemical treatment	Raw tannery wastewater	2810	COD removal (70 %), Electric current (15.0 W), Time (10 min) and pH (3)
Pokrywiecki Sauer et al. (2006)	UV/H ₂ O ₂	Coagulated tannery wastewater	200–800	COD removal (60 %), H ₂ O ₂ (0.5 h L ⁻¹), Time (4 h)
Schrank et al. (2005)	Fenton reagent	Coagulated tannery wastewater	130	COD removal (80 %), H ₂ O ₂ /Fe ²⁺ (500/100 w/w), Time (2 h)
Schrank et al. (2004)	Photocatalysis (UV/TiO ₂)	Coagulated/ Flocculated tannery wastewater	2365	COD removal (6 % at pH 3), TOC removal (11 % at pH 3), BOD removal (15 % at pH 7)
Dogruel et al. (2004)	Ozone	Biologically treated tannery wastewater	835	COD removal (30 %), Ozone flow rate (42.8 mg min ⁻¹), Time (5 min)
Dantas et al. (2003)	Fenton reagent	Raw tannery wastewater	1803	COD removal (70 %), Time (20 min), pH (2.5) and Temperature (25 °C)

Despite of a broad range of applications, AOPs also have some drawbacks that should also be considered before its applications. The presence of scavenger compounds such as an excess amount of H₂O₂ sometime can act as a hydroxyl scavenger instead of hydroxyl radical source, which interferes with the COD determination and reduces the reaction kinetics making the process uneconomical (Kang 2002; Lofrano et al. 2013). Further, the TWW also contains a significant amount of chromium, which may be oxidized from trivalent to hexavalent form, a more toxic form during oxidation treatment and thus, it is highly recommended to evaluate the possible effects of oxidation on the transformation of chromium atoms in different oxidation states (De Laat et al. 2004; Dogruel et al. 2006; Rameshraj and Suresh 2011; Lofrano et al. 2013). For these reasons, AOPs should be applied more properly to the segregated streams of wastewater containing high amount of aromatic compounds for fenton treatments or high content of salts for electrochemical treatment.

Moreover, AOPs still have not been put commercially at large scale (especially in the developing countries) even upto today mostly because of the relatively high costs. Nevertheless, their high oxidative capability and efficiency make AOPs popular techniques for the tertiary treatment of recalcitrant organic and inorganic pollutants. The increasing interest in wastewater reuse and more stringent regulations regarding the water pollution prevention and control are currently accelerating the implementation of AOPs at large scale.

5.4 Combinatorial Treatment Approaches

In the previous section, various treatment approaches applied for TWW have been discussed. However, these treatment approaches have some serious limitations that need to be addressed further. The presence of residual organics, dyes, and other impurities in TWW even after the biological treatment processes followed by the RO based membrane technologies have been reported as the major drawbacks leading to membrane fouling and finally failure of treatment processes (Srinivasan et al. 2012). Therefore, a combined application of physico-chemical treatment methods with biological treatment methods or various oxidation processes is generally preferred for the effective TWW treatment. Some of the combined treatment methods applied for TWW is presented in Table 6.

Table 6 Combined treatment approaches reported for tannery wastewater

References	Combined treatment applied	Pollutants	Optimum parameters
Suganthi et al. (2013)	Hybrid membrane bioreactor	COD and Color	Electric current density (15 mA/cm ²), Electrocoagulation time (15 min), Membrane area (0.0143 m ²), Membrane spacing (0.22 μm), pH (7.4 and 9)
Srinivasan et al. (2012)	Biological treatment with ozonation	COD and color	Ozone flow rate (3 g/h), Time (24 h), pH (12), Hydraulic retention time (36 h), sludge age (10 days)
Mandal et al. (2010)	Biological treatment with fenton oxidation	COD, BOD, Chromium, Sulphide and Color	Fenton reagent (6 g FeSO ₄ and 266 g H ₂ O ₂), Time (30 min: fenton oxidation, 72 h: biological oxidation), pH (2.5), Temperature (30 °C)
Iaconi et al. (2009)	SBBR with ozonation	COD, BOD, TSS, TKN and color	Sludge production (0.4 kg TSS/kg COD), Time (5760 and 2160 h)
Rodrigues et al. (2008)	Photo-electrochemical treatment with electro dialysis	COD and NH ₄ -N	Electric current density (36 mA/cm ²), Ti electrode, Membrane area (1.72 dm ²), Membrane spacing (0.75 mm)
Dogruel et al. (2006)	Biological treatment + ozonation with biological treatment	COD	Ozone flow rate (20 g/h), Reaction time (30 min)
Naumczyk and Rusiniak (2005)	AOP with fenton reagent	COD and Ammonia	Fenton reaction time (30 min)
Szpyrkowicz et al. (2005)	Electrochemical treatment with biological treatment	COD and Ammonia	Sludge production (1.37 kg/m ³ /day), Electrolysis time (49 min)

(continued)

Table 6 (continued)

References	Combined treatment applied	Pollutants	Optimum parameters
Kennedy et al. (2004)	CAACO system	COD, BOD, Sulphide and sulfate	Volumetric loading rate ($0.7376 \text{ m}^3/\text{m}^3$ day), Surface loading rate ($0.2438 \text{ m}^3/\text{m}^3/\text{day}$)
Iaconi et al. (2004)	SBBR with ozone oxidation	COD, TKN and TSS	Sludge production ($0.05 \text{ kg VSS/kg COD}$)
Iaconi et al. (2003)	SBBR with ozonation	COD, TKN and TSS	Sludge production (4 kg/kg COD), Organic loading ($2.6 \text{ kg COD/m}^3/\text{day}$)
Di Iaconi et al. (2002)	SBBR with ozone oxidation	COD, Ammonia and SS	O_3 flow rate ($8.7 \text{ mg O}_3/\text{min}$), Sludge production (4 kg TSS/kg COD)

6 Waste Minimization, Operation, Treatment and Management in Leather Industries

6.1 Solid Waste Generation, Treatment and Management

In LIs, apart from liquid waste, a large amount of chromium containing tanned solid waste (non-biodegradable sludge) is also generated during leather processing (Dixit et al. 2015). The waste generated finds very limited applications and its disposal causes serious environmental problems (Mwinyihija 2010, 2012). The types and quantity of solid waste generated during the processing of 1 t of raw hide/skins have been presented in Table 7.

However, the conventional treatment and disposal of solid waste is not environmentally feasible because of transformation and leaching of Cr(III) from tanned waste to Cr(VI) and groundwater, emission of nitrogen oxide (NO_x), hydrogen cyanide (HCN) and ammonia (NH_3) (Fathima et al. 2012; Dixit et al. 2015). Therefore, the combination of aerobic treatment (for degradation of low molecular weight compounds) with anaerobic treatment (for further degradation of metabolites) may be a suitable treatment option for tannery waste. The methodologies for the treatment of liquid tannery waste using solid tannery waste have been recently discussed by Fathima et al. (2012). Further, after treatment the remaining waste can be recycled and utilized as useful by products and raw materials. Some of the technological options, which are proposed for the handling and management of solid waste, are presented in Fig. 1.

Table 7 Nature and quantity of solid waste generated during the processing of 1 t of raw hide/skins

Nature of solid waste generated	Quantity (kg)
Salt from handshaking	80
Salt from solar pans (not realized)	220
Hair (pasting ovine)	100
Raw trimmings	40
Lime sludge (mostly bovine)	60
Fleshing	120
Wet blue trimmings (grain splits)	30
Chrome splitting (bovine)	65
Chrome shaving (mostly bovine)	95
Buffing dust (including shaving bovine after crust)	65
Dyed trimmings	35
Dry sludge from CETPs	125

Adapted from Rao et al. (2004) and Thanikaivelan et al. (2005)

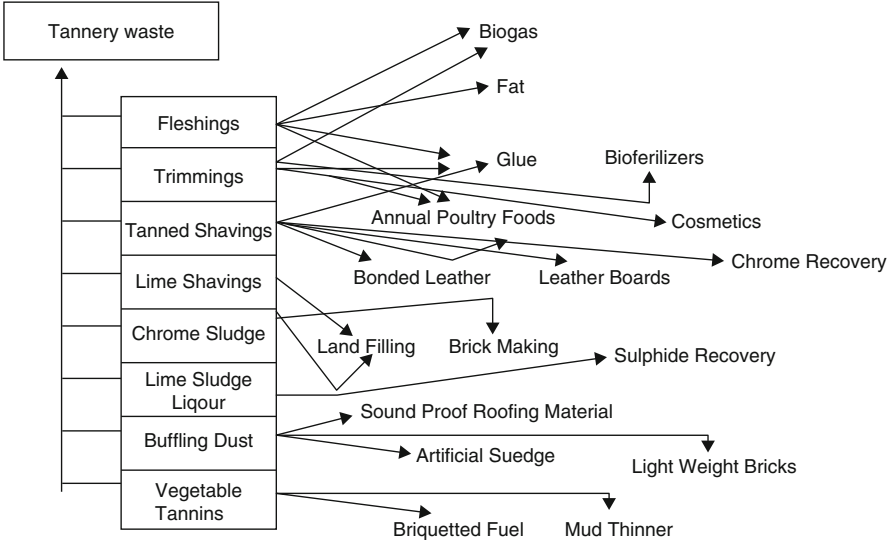


Fig. 1 Technological options for handling and management of solid waste generated during leather production (adapted from ILTIP 2010)

6.2 Gaseous Emission and Control

The emission of gaseous waste such as ammonia (during deliming, unhairing and drying), hydrogen sulphide (released in TWW from sulphides if pH is >8), particulate matter (containing chromium from reduction of chromate or from buffing), and volatile organic compounds (hydrocarbons, amines and aldehydes) from LIs during the different steps of tanning processes may also cause atmospheric pollution (Dixit et al. 2015). Therefore, the proper control of gaseous emission should be required.

6.3 *Clean Technologies for Hazards Minimization*

Environmental pollution due to LIs is a major cause of concern and its mitigation requires some cleaner technologies (CTs) or also regarded as greener technologies (GTs) for pollution prevention and hazards minimization. CTs utilize the processes that avoid the use of harmful chemicals or promote the use of eco-friendly chemical and cut or eliminate the gaseous emissions and wastes and therefore are cost-effective. Various CTs for the tannery waste minimization and control have been reviewed by many workers (Thanikaivelan et al. 2005; Lofrano et al. 2013; Islam et al. 2014; Dixit et al. 2015).

The development and implementation of CTs at large scale require (a) careful auditing and assessment of the toxicological effects of chemicals used in leather processing, (b) to avoid the use of environmentally susceptible chemicals, (c) to ensure the maximum uptake of chemicals used, (d) assessment of environmental impact of waste generated during leather processing, and (e) optimization of processes for the best economic returns. However, the success of CTs depends on the following parameters: (a) reduction of pollution load in terms of quantity and quality, (b) tanner's benefit in terms of leather quality and/or cost reduction, (c) reproducibility of the process, (d) economic feasibility of process (e) wide market opportunities. Further, the use, assessment and selection of best available techniques (BAT) for the tanning of hides and skins have been discussed (IPPC 2013).

7 International Legislations Scenario for Tannery Wastewater and Chemicals

7.1 *Legislations for Discharge Limits of Tannery Wastewater*

In developing countries, according to the environmental pollution control regulations set by various national and international environment protection agencies, LIs are forced to set up the WWTPs either individually as ETP or collectively as CETP and the treated wastewater should comply with the discharge standards. The compliance with the discharge standards has not always been practical either because the laws are too ambitious or unrealistic in case of certain parameters, or they have lacked the effective instrumentation and institutional support. Some environment protection laws have not succeeded because they do not match the technical requirements and economic reality of the country or they do not have the institutional support to implement them into consideration.

In India, during the 1990s, several LIs were ordered to close their units as these could not meet the discharge standards, while many of them paid huge compensation for the damage caused due to the groundwater contamination (CSIRO 2001). For the sake of LIs, the Indian government has offered subsidies to construct

Common Effluent Treatment Plants (CETPs) for the treatment of TWW. Notwithstanding, the pollution problems are still common due to high operation and management cost associated with CETPs and thus causing illegal dumping of wastewater (Beg and Ali 2008). In Uganda, the main leather industry was found to dump its wastewater directly into a wetland adjacent to Lake Victoria (The Monitor 2009) whereas in Croatia, the pollution abatement cost exceeded the compensation cost against the irresponsible behaviour of LIs (EcoLinks 2001).

The environmental pollution due to the discharge of TWW has become a serious concern in recent years. For pollution prevention from TWW and its chemicals, the United Nations Industrial Development Organization (UNIDO) has compiled the standard limits for the discharge of TWW into water bodies and sewers from several countries worldwide (UNIDO 2000, 2003). The discharge standards for some of the countries are presented in Table 8. The discharge limits for TWW may vary from country to country and are either related to the quality of treated wastewater or the quality of receiving water bodies (Dixit et al. 2015).

7.2 *Legislations for Leather Chemicals*

A variety of chemicals are used during the leather processing, which are highly toxic to living beings and cause environmental pollution. In this view, some countries have also made regulations for the production, import and sale of leather products containing harmful chemicals. The chemicals and their permissible limits in leather and leather products approved in some countries are summarized in Table 9. However, the European Chemical Agency (ECHA) has also prioritized and restricted the use of a few chemicals in LIs under Substances of Very High Concern (SVHC), which are considered to be hazardous for environment and human beings (UK REACH 2009). However, all the chemicals are still used in leather making and therefore their proper control is urgently required.

8 **Challenges and Future Prospects**

Today's the LIs are facing some serious challenges posed by the public and governments mainly due to the environmental pollution and there is a public outcry against the industry. The major challenges faced by LIs include:

- (a) Increased cost of leather production per unit area due to the stringent environmental regulations.
- (b) Increasing demand of raw material i.e. raw hides, skins and semi-finished leathers.
- (c) Lack of advanced processing techniques and waste treatment technologies in developing countries.

Table 8 Discharge limits for tannery wastewater into water bodies and sewers in some countries

S. No.	Parameter	Italy		Turkey		Netherlands		Argentina		Brazil		Egypt		China		Vietnam		Indonesia		Bangladesh		India		Pakistan	
		S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	*S ^a	S ^b	S ^a	S ^b	S ^a	S ^b
1.	pH	5.5-9.5	5.5-9.5	6-9	6-10	6-10	6.5-10.0	5.5-10	5.5-10	5.0-9.0	5.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	5.5-9.0	5.5-9.0	6.0-9.0	6.0-9.0			5.5-9.0	5.5-9.0	6.0-9.0	6.0-9.0
2.	Temperature °C	30-35	30-35				40	45	45	<40	40	35	0		35	40	45					40-45	40-45	40	
3.	Conductivity (µS/cm)																								
4.	Suspended solids (mg/L)	40-80	200	150	350	150	350					30	500	70-150	400	100	200	150	150	500		100	600	200	
5.	Settleable solids							0.5	0.5	1.0		a	5-10		10										
6.	BOD ₅ (O ₂ mg/L)	40	250	100	250	5	250	50	200	60		20-30	400	20-100	600	50	100	150	150	250		30	500	80	
7.	COD (mg/L)	160	500	200	800	a	a	250	700			30-40	700	100-300	1000	100	400	300	300	400		250		150	
8.	TDS (mg/L)											800-1200	2000									2100	2100		
9.	Sulphide (S ²⁻) (mg/L)	1	2	1	2	a	a		1	0.2	5	1	10	1	10	0.5	1.0			2.0		2	2	1	
10.	Chrome (III) (mg/L)		4				1				5			1.5	2.0	1.0	2.0					2	2		
11.	Chrome (VI) (mg/L)	0.2	0.2	0.3		a	a							0.5	0.5							0.1	0.1		
12.	Total Chrome (mg/L)	2	4	2	5	0.05	2	0.5	2	0.5		0.05	5-10	1.5	1.5	2.0	2.0	2	2	2.0		2	2	1	
13.	Chloride (mg/L)	1200	1200			200	a	a	a			a	a									1000	1000	1000	
14.	Sulfates (mg/L)	1000	1000			1700	3	a	1000			a	a									1000	1000	1000	
15.	Ammonia (mg N/L)	10-15	30					3	10	5		100	100					10	10			50	50	40	
16.	TKN (mg N/L)			100		a	a	10	30	10		a	a			60	60								

(continued)

Table 8 (continued)

S. No.	Parameter	Italy		Turkey		Netherlands		Argentina		Brazil		Egypt		China		Vietnam		Indonesia		Bangladesh		India		Pakistan	
		S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	S ^a	S ^b	*S ^a	S ^b	S ^a	S ^b	S ^a	**S ^b
17.	Phosphorous (mg PL)									1															
18	Oil/grease (mg/L)	20	40	20	100			100	100	20–30	100	100	100	100	10–15	100	10	30	5	5	20	10	20	10	
19.	Phenol (mg/L)	0.5	1		10	^a	^a	0.5	0.5	0.1–0.5	0.001–0.002	0.001–0.002		^a	0.5	2.0			1			5–50	5–50	0.3	
20.	Detergents (mg/L)																		1.5						
21.	Solvents (mg/L)																								
21.1.	Hydrocarbons (mg/L)	0.2	0.4																						
21.2.	Nitrogenous (mg/L)	0.1	0.2																						
21.3.	Chlorinated (mg/L)	1	2					1	2	5															

S^a: Surface, S^b: Sewer, *S^a: Bangladesh has no discharge standards for tannery wastewater into surface water, **S^b: Pakistan has no discharge standards for tannery wastewater into sewer

^aSpaces left blank indicate that parameters which are not specified and considered as specific requirements that need to be fulfilled

Table 9 Maximum permissible limits of chemicals of leather products in some countries (adapted from Dixit et al. 2015)

Residual substances limits for chemicals	European Union	Germany	Austria	Denmark	France	Netherlands	Switzerland
Azodyes ^a	30 ppm						
Pentachlorophenol	30 ppm	5 ppm	30 ppm		30 ppm	30 ppm	30 ppm
Phthalates	0.1 %	0.1 %		0.05 %			
PCBs and PCTs ^b	Not to be used						
Biocides ^c	5 ppm	5 ppm	5 ppm		5 ppm	5 ppm	10 ppm
Hexavalent Chromium	3 ppm	10 ppm					
Cadmium	100 ppm		75 ppm			100 ppm	100 ppm
Arsenic	Nil						
Lead	90 ppm						
Organotin Compounds	Nil						
Specific Flame Retardants	<0.1 %						
Formaldehyde		>1500 ppm	>1500 ppm		200–400 ppm	120 ppm	

^aAzo dyes: Biphenyl-4-ylamine; 4-aminobiphenyl xenylamine; Benzidine; 4-Chloro-o-toluidine; 2-Naphthylamine; o-aminoazotoluene; 4-amino-2',3-dimethylazobenzene; 4-o-tolylazo-o-toluidine; 5-Nitro-o-toluidine; 4-chloroaniline; 4-methoxy-m-phenylenediamine; 4,4'-methylenedianiline; 3,3'-dichlorobenzidine; 3,3'-dimethoxybenzidine o-dianisidine; 3,3'-dimethylbenzidine 4,4-bi-o-toluidine; 4,4-methylenedi-o-toluidine; 6-methoxy-m-toluidine; p-cresidine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-oxydianiline; 4,4'-thiodianiline; o-toluidine; 2-aminotoluene; 4-methyl-m-phenylenediamine; 2,4,5-trimethylaniline; o-anisidine 2-methoxyaniline; 4-amino-azobenzene

^bPCBs: Polychlorinated biphenyls; PCTs: Polychlorinated terphenyls

^cBiocides (23 approved): Human hygiene biocidal products; Private area and public health area disinfectants and other biocidal products; Veterinary hygiene biocidal products; Food and feed area disinfectants; Drinking water disinfectants; Preservatives; In-can preservatives; Film preservatives; Wood preservatives; Fibre, leather, rubber and polymerised materials preservatives; Masonry preservatives; Preservatives for liquid-cooling and processing systems; Slimicides; Metalworking-fluid preservatives; Pestcontrol; Rodenticides; Avicides; Molluscicides; Piscicides; Insecticides, acaricides and products to control other arthropods; Repellents and attractants; Other biocidal products; Preservatives for food or feedstocks; Antifouling products; Embalming and taxidermist fluids; Control of other vertebrates

- (d) Lack of specific dedicated industrial areas for the positioning of LIs.
- (e) Poor capacity utilization leading to the higher financial cost and overheads charges.
- (f) Lack of financial support from government.

The mitigation of these challenges requires the financial support at large scale from the government for the upgradation of LIs, especially small scale industries (Xu and Zhiping 2011). Hence, there is a need to revisit the leather processing again for making the continued sustainability of LIs in near future because LIs are the key drivers of many nation's economy.

9 Summary and Conclusion

- (a) LIs are one of the major sources of environmental (soil, water, air) pollution.
- (b) TWW is a highly polluted wastewater among all the industrial wastewater.
- (c) Currently, the processes used for leather making in several developing countries are traditional and required to be optimized for chemical and water consumption.
- (d) The search for some other suitable tanning agents to replace the chromium is urgently required for eco-sustainable tanning process.
- (e) Sulfide is highly toxic but the mechanism of toxicity is not well understood and implementation of adequate technology for H_2S desorption is required.
- (f) Membrane bioreactors and constructed wetlands are the eco-friendly options for the treatment of TWW and its management, but have some limitations that need to be addressed in the future.
- (g) The combinatorial approaches involving physical or chemical with biological treatment process to treat the TWW may give satisfactory results as compared to the individual treatment process.
- (h) The emerging treatment approaches like membrane filtration and oxidation processes are also currently using/under analysis.
- (i) AOPs are much promising to remove the recalcitrant organic pollutants but there is a still need to optimize these for best economic returns.
- (j) The emerging anammox technology for the anaerobic removal of ammonia from TWW is under research and further investigation is required.
- (k) A complete understanding of toxicity profiles of TWW may also be helpful in achieving the appropriate treatment solutions for future tanneries.
- (l) Locating LIs in a planned industrial area is another common approach to abate the environmental pollution in parallel to strengthen the discharge limits for TWW.
- (m) The use of eco-friendly chemicals, water minimization technologies and wastewater treatment/purification and recycling as per the EU integrated pollution prevention strategy and greening policy will be fruitful for solving the environmental problems.

Thus, we can say that there is no treatment method at its best to treat TWW and its chemicals. However, it is clear that continuous efforts are required in order to search for the better treatment approaches for TWW in near future. Further, the emerging treatment approaches like AOPs in combination with biological treatment processes will remain an agenda for the policy makers and water sector professionals to apply the best pollution prevention solution for the future tanneries.

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