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Membrane technology in tannery wastewater management: A review

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ABSTRACT

The leather industries is a key and viable sector of the economy of many emergent countries, but it is also recognised as one of the highest polluting industries. This is as a result of the discharge of vast amounts of chemical containing water employed in the leather making process into the environment with little or no treatment. Nearly 40-45 litres of water are used per kilogramme of raw hide processed into finished leather. However, of the total amount of water employed in the leather making process approximately 90% is discharged into the environment as effluent. As such, a large amount of noxious effluent is produced having huge chemical oxygen demand and biochemical oxygen demand, suspended and dissolved solids, chromium, surfactants and other toxicities. It is therefore vital to adequately treat/detoxify the tannery wastewater for environmental safety. Various methods are available for the treatment of tannery wastewater. The numerous physiochemical techniques used for wastewater treatment can also be applied to tannery wastewater (to the entire process or to individual step in the process). However, conventional treatment methods have certain limitations in real field of tannery wastewater treatment arena. Membrane technologies gain importance in this regard. This paper provides an insightful review on the environmental pollution and toxicity characteristics of tannery wastewater and chemicals. Moreover, traditional treatment methods, their advantages and disadvantages, for tannery wastewater are briefly discussed. Membranes, their classifications and available preparation techniques are briefly reviewed. Finally, advances in the membrane treatment approaches used for the treatment and/or detoxification of tannery wastewater at both laboratory and pilot/industrial scale are evaluated. In addition, integrated membrane treatment approaches alone or in combination with physicochemical and biological treatment approaches are also considered.

Keywords: Environmental pollution; Leather Industry; Membrane technology; Wastewater characteristics

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1.1 Introduction

The leather industry is a viable sector of the world economy, and although not amongst the largest industrial segments worldwide, it can be a dominant regional player in certain areas. Tanning is recognised as one of the oldest industrial practices in the world. The tanning process aims to transform skins into a stable product namely leather as well as to arrest the decaying process. The tanning process can be represented in three major phases, that is, the procurement and pre-treatment of raw animal hides; the actual tanning of hides with an appropriate tanning agent; and lastly the drying and finishing the hides before sending them to end product manufacturers. The two main types of tanning are mineral tanning and vegetable tanning, with mineral tanning in the form of chrome tanning still constituting the vast majority of the industry(Bosnic et al., 2000, Buljan et al., 2011, Chowdhury et al., 2013b, Tsotsos, 1986, Gutterres et al., 2015, Islam et al., 2014, De Nicola et al., 2007, Song et al., 2000, Hu et al., 2011, Dixit et al., 2015, Dutta, 1985, Saxena et al., 2016).

The leather making process employs a significant amount of water. This is because hides are converted into leather in aqueous mediums containing acids, alkalis, tannins, oils, fats and salts, and other chemicals. Nearly 40-45 litres of water are used per kilogramme of raw hide processed into finished leather. However, of the total amount of water employed in the leather making process approximately 90% is discharged into the environment as effluent (Gutterres et al., 2015, Islam et al., 2014, Buljan et al., 2011, Krishnamoorthi et al., 1970, Dutta, 1985, Saxena et al., 2016).

As such, a large amount of noxious effluent is produced having huge chemical oxygen demand and biochemical oxygen demand, suspended and dissolved solids, chromium, surfactants and other toxicities(De Nicola et al., 2007, Coast et al., 2008, Durai and Rajasimman, 2011, Azom et al., 2012, Jahan et al., 2014, Nazer and Siebel, 2006, Wang et al., 2016, Jang et al., 2017, De Gisi et al., 2009, Kiril Mert and Kestioglu, 2014). The difficulty in treatment of tannery wastewater is due to the complexity and broad nature of the industry as well as the large amounts of chemicals employed in the leather processing. The segregation of each sectional stream and separate treatment therefore requires very high investments in terms of equipment, land etc. (Buljan et al., 2011, Lofrano et al., 2013).

Various methods are available for the treatment of tannery wastewater (Lofrano et al., 2013). The numerous physiochemical techniques used for wastewater treatment can also be applied to tannery wastewater (to the entire process or to individual step in the process) but these processes may be expensive. The different treatment operations are dictated by the level of contamination in the water, which is directly related to the production process, the legal compliance for water discharge and the possibility of sending the water to a communal wastewater treatment plant or municipal collector or the possibility of reutilisation in the production process (Durai and Rajasimman, 2011, Goswami and Mazumder, 2014, Ramanujam et al., 2009, Chowdhury et al., 2013b).

Wastewater treatment generally encompasses physicochemical and biological processes as well as a combination of both (Ramanujam et al., 2009, Grady Jr et al., 2011, Droste and Gehr, 2018, Lofrano et al., 2013, Durai and Rajasimman, 2011, Tare et al., 2003). Conventional methods available for wastewater treatment include aerobic treatment, anaerobic treatment, chemical wastewater treatment (chemical precipitation), chemical oxidation, ozonisation, electrochemical method and physical methods (mechanical treatment) (Barman et al., Buljan et al., 2011, Durai and Rajasimman, 2011, Tsotsos, 1986, Coast et al., 2008, Elabbas et al., 2016, Deghles and Kurt, 2016, El-Sheikh et al., 2011). There are situations in which an individual tannery may choose to apply all the afore-mentioned water treatments on site. In this instance, treatment of tannery wastewater may involve separation of tanning yard and soaking wastewater from the remaining streams, chemical treatment of tanning yard wastewater for precipitation of chromium, physical treatment of chloride laden soaking wastewater and finally biological treatment of the rest. However in some cases tanneries may choose to carry out a pre or part- treatment of the effluent before it is sent off to a central or municipal treatment plant. It is however important to note that at least some treatment should be carried out to the effluent because of its high level of toxicity(Buljan et al., 2011).

However, conventional treatment methods have certain limitations in real field of tannery wastewater treatment arena. Biological treatment methods give rise to an excessive production of sludge whereas physical and chemical methods are too expensive in terms of energy and reagent costs. In addition due to complexity of the tannery effluents, most of the traditional methods are often found inadequate for meeting stringent requirement of discharge standard. Those also appear to be uneconomic in terms of treatment cost per unit volume of wastewater per day. It may also be worth mentioning that in many research studies carried out on tannery wastewater treatment processes, it has been shown that an integrated application of combined process of physical and chemical with the biological process to treat tannery effluents would give satisfactory results as compared to individual treatment processes. This may be attributed to the fact that wastewater emanating from various sub-processes of tannery operations show variable characteristics therefore differential treatability (Kowalik-

Klimczak and Gieryoz, 2014, Durai and Rajasimman, 2011, Stoller et al., 2013, El-Sheikh et al., 2011, Droste and Gehr, 2018, Jahan et al., 2014, Krishnamoorthi et al., 1970)

Table 1. Advantages and disadvantages of conventional effluent treatment methods(Kowalik-Klimczak and Gieryoz, 2014)

Method	Advantages	Disadvantages
Precipitation	– the possibility of reducing the concentration of chromium (III) in the wastewater to the level of 20–50 g/dm3	– satisfactory efficiency for the concentration of chromium (III) in the wastewater above 10 g/dm3 – poor quality of the recovered chromium (III) due to the presence of impurities
Biological methods	– reduction of chromium (III) up to about 94%	– the necessity to maintain the pH of the effluent within the range of 6–9 – a difficult and prolonged period of sludge inoculation
Ion exchange	– very good durability and ease of regeneration of the ion exchange bed	– the need for the oxidation of chromium (III) to chromium (VI) prior to the process – Bath devoted to the ion exchange column should contain no more than 0.1 g CrO3/dm3
Carbon adsorption	– selectivity with respect to anions offering the possibility to use it for the purification of solutions containing, for example, sulphate, chloride or bicarbonate anions	– low sorption capacity of activated carbon and the need for its frequent regeneration
Solvent extraction	– high efficiency	– the need for large amounts of extractable organic substances, which are often toxic and flammable

1.2 Characteristics of tannery waste water and its effects on the environment

The tanning process is different according to the required properties in the end product and as such, the kind and amount of waste produced varies in a wide range. The characteristics of tannery effluent vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for a specific process, amount of water used, process of hide preservation, in-plant measures to control pollution as well as the type of final product produced by a tannery (Gutterres et al., 2015, Abdalla et al., 2016, Sundar et al., 2001, Rao and Singh, 2013, Song et al., 2000, Wang et al., 2016). There are four major groups of sub-processes required to make finished leather: beam-house operation, tan-yard processes, re-tanning and finishing. Traditionally in most tanneries processing of leather begins from the de-hairing process right down to the retanning processes. However in some instances only pre-pickled leather is processed with a retanning process (Sundar et al., 2001, karabay, 2008, Das et al., 2007a, Przywara, 2017, Chowdhury et al., 2013a, Islam et al., 2014).

The first operation of the tannery unit is beam house process by which the hides/ skins are dressed for tanning. It is divided into different sub-processes consisting of soaking, liming and unhairing, deliming, and bating. Soak liquors contain suspended solids, dirt, dung, blood adhering to hides and skins, and chloride etc. whilst lime liquors are highly alkaline. This stream contains suspended solids, dissolved lime, sodium sulphide, high ammoniacal nitrogen and organic matter. Unhairing and fleshing effluent contains fatty fleshing matter in suspension. The spent deliming liquors carry significant BOD load. The spent bate liquors on account of presence of soluble skin proteins and ammonium salts containing high organic matter. Pickle liquors are acidic and contain high amount of salt. In summary, these operations lead to discharge of high amount of sulphides, lime, ammonium salts, chlorides, sulphate, and protein in the effluent. In addition, the wastewater from these processing steps is characterized with a high amount of BOD and COD as well as a high TKN value (karabay, 2008, Bosnic et al., 2000, Buljan et al., 2011, Das et al., 2007b, Cassano et al., 1997, Ates et al., 1997, Nazer and Siebel, 2006, Wang et al., 2016, Camargo and Alonso, 2006).

Tan yard operations aim at stabilising the hide and this is achieved through a number of treatments with a variety of tanning agents. Tanning agents can be categorised into 3 main groups: mineral tanning agents (chrome, titanium, aluminium etc.), vegetable tanning agents (polyphenolic compounds leached from vegetables) and alternative tanning agents (syntans, aldehydes and oil tanning agents) (Sundar et al., 2001, Cassano et al., 1997). The choice of tanning method and the agent depends chiefly on the properties required in the finished leather, cost of material and type of raw material. A significant percentage of tanneries, approximately 80-95%, use trivalent chromium salts in their tanning operations. The spent chrome liquors contain high concentration of chrome compounds and neutral salts (belay, 2010b, Vinodhini and Sudha, 2016, Bosnic et al., 2000, Tadesse and Guya, 2017).

The wastewater from neutralization, retanning, dyeing and fatliquoring sections contribute little pollution load (Bosnic et al., 2000). In contrast to this neutralization section had very low COD. The reason for this low COD value may be due to the use of neutral salts and this step is just added up for the washing of the chrome tanned hides. Effluents of this section containing low concentration of chemically oxidisable materials. This fact justified the low COD results. However, if fat liquor exhaustion is poor some fatty substances may be produced through inter-reaction when waste waters mingle. Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulsify, they create a very high oxygen demand on account of their bio-degradability. During the coloration process a large percentage of the synthetic dye does not bind and is lost to the waste stream. Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly coloured and aesthetically unpleasant. The effluent from leather industries thus carries a large number of dyes and other additives which are added during the colouring. These are challenging to remove in conventional water treatment procedures and can be transported easily through sewers and rivers especially because they are intended to have high water solubility. They may also undergo degradation to form products that are highly toxic and carcinogenic. Thus dyes are a potential hazard to living organisms (Bosnic et al., 2000, Buljan et al., 2011, Padhi, 2012, Mottalib et al.) . Table 2 summarises some of the characteristics that can be expected in tannery wastewater.

Table 2: Summary of Tannery Wastewater Characteristics (Bosnic et al., 2000, Buljan et al., 2011)

Tannery unit process	Wastewater characteristics
Soaking	Hyper saline waste water contains large amounts of dissolved solids
Fleshing	Dissolved solids, suspended solids and biodegradable organics and nutrients
Liming	Large amount of biodegradable organics, TKN, Ammonia, high conductivity
Deliming	Biodegradable organics, TKN, dissolved organic and inorganic salt
Pickling	Acidic wastewater contains dissolved salt, high conductivity
Chrome tanning	Chrome bearing, acidic wastewater
Finishing operations	High colour, organic matter, surfactants, chromium

1.2.1 Environmental impacts of tan-yard effluents

The major public concern over tanneries has usually been about odours and water pollution from untreated discharges. Important pollutants linked with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides as addition to trace organic chemicals and increasing use of synthetic chemicals such as pesticides, dyes and finishing agents, as well as from the use of newer processing chemical solvents. These substances are frequently toxic and persistent, and affect both human health and the environment (Abdalla et al., 2016, ALeixandre et al., 2011, Barman et al., belay, 2010b, Bhattacharya et al., 2013, Bosnic et al., 2000, Buljan et al., 2011, Chowdhury et al., 2013b, Das et al., 2007b, Durai and Rajasimman, 2011, El Khalfaouy et al., 2017, Fababuj-Roger et al., 2007, Goswami and Mazumder, 2014, Gutterres et al., 2015, Islam et al., 2014, karabay, 2008, Kowalik-Klimczak and Gieryoz, 2014, Ramanujam et al., 2009, Rambabu et al., 2017, Rambabu and Velu, 2016, Ranganathan and Kabadgi, 2011, Rao and Singh, 2013, Scholz et al., 2005, stoller, 2017, Stoller et al., 2013, Sundar et al., 2001, Suthanthararajan et al., 2004, Tsotsos, 1986, Velu et al., 2017, Velu et al., 2015, Vinodhini and Sudha, 2016, Chowdhury et al., 2013a, Tadesse and Guya, 2017, Azom et al., 2012, Alam et al., 2010).

Many components in effluents are broken down by bacterial action into more simple components. Oxygen is required for both the survival of these bacteria (aerobic bacteria) and the breakdown of the components. Depending on their composition, this breakdown can be quite rapid or may take a very long time. If effluent with a high oxygen demand is discharged directly into surface water, the sensitive balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen dependent plants, bacteria, fish as well as the river or stream itself to die. The outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions (Bosnic et al., 2000, karabay, 2008).

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations). These sources of nitrogen pose two direct problems. The first problem being that presence of high levels of nitrogen over-stimulate growth in plants. Water-based plants and algae grow too rapidly, whereupon waterways become clogged and flows are impaired. As the plants die, a disproportionately high amount of organic matter has to be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop (Carpenter et al., 1998, Howarth, 2008, Camargo and Alonso, 2006). The second problem associated with nitrogen in tannery effluents is that the nitrogen released through protein breakdown and the deliming process is in the form of ammonia. The latter can be converted by bacteria over several stages into water and nitrogen gas which is ultimately released into the atmosphere. Both of these breakdown products are non-toxic, yet large volumes of oxygen are needed in the process. If oxygen demand is greater than the level supplied naturally by the water course, toxic anaerobic conditions can rapidly develop (Durai and Rajasimman, 2011).

Chlorides are introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system and may ultimately end up in the ground water. High salt contents are only tolerable if the effluents are discharged into tidal/marine environments(Bosnic et al., 2000, karabay, 2008, Buljan et al., 2011).
The major concern of pollution in chrome tannery unit is envisaged for chromium, which is prevalent in two states - the trivalent (Cr3+) and hexavalent (Cr6+) state respectively. If chrome discharges are in excess, chromium might remain in solution. It is already observed from earlier research work that hexavalent chromium is very much carcinogenic for human being upon long time exposure(stoller, 2017, Belay, 2010a). The toxicity and carcinogenic effect of chromium (VI) is perceived after it enters into living cell. Several in-vitro studies revealed that high concentrations of chromium (VI) in the cell could lead to DNA damage, causing several genotoxic insults to the human body. Besides this, chromium salts (chromates) also cause allergic reactions in human body. It is also observed that even in low concentrations, chromium has a toxic effect upon daphnia thus disrupting the food chain for fish life. Both forms of chromium are toxic to plants. It has been found that they inhibit germination, reduce growth, generate oxidative stress, decrease protein content, inhibit photosynthesis and alter enzyme activities in the exposed plant (Sundar et al., 2001, Velu et al., 2017, Velu et al., 2015, Vinodhini and Sudha, 2016, Belay, 2010a, belay, 2010b, Cieślak-Golonka, 1996, Barrera-Díaz et al., 2012, Sinha et al., 2006, Armienta et al., 2001, Hafez and El-Mariharawy, 2004).

Solvents and dyes originate from degreasing and finishing operations. These also have an adverse effect on the environment if disposed of without further treatment. Solvents in effluents discharged to surface waters can form a microfilm on the water surface, thus inhibiting the up-take of oxygen. Solvents break down in a variety of ways; some inhibit bacterial activity and remain in the eco-system for extended periods of time (Bosnic et al., 2000). In addition to being toxic, dye effluents also contain chemicals that are carcinogenic, mutagenic or teratogenic to various organisms. This is especially serious because many chemicals can cause damage to genetic material without being expressed immediately (Padhi, 2012, Mottalib et al.).

1.3 Membrane Processes

The insufficiencies in the traditional wastewater treatment methods have sparked much interest in novel methods of water treatment such as membrane technology. Membranes hold great potential in advancing water and wastewater treatment to improve the efficiency of impurities removal as well as to augment water supply via safe use of un-conventional water resources. Membrane technologies for water purification as well as effluent treatment have been actively pursued for decades, but with recent innovation of both analytical and fabrication tools, more advanced membrane technologies are surfacing. These technologies, in particular, have proven viable in water purification with decades of productive use. Membrane technology is a physical process for the separation of material mixtures in which the membranes function much like a filter. Of importance to note, the separated substances are neither thermally nor chemically nor biologically modified. In recent years membrane technologies have been developing rapidly and their cost is continuing to reduce while the application possibilities are ever extending (Cassano et al., 1997, Bilstad, 1997, Sagle and Freeman, 2004, stoller, 2017, Stoller et al., 2013, Tylkowski and Tsibranska, 2015).

A membrane is a thin physical interface that moderates certain species to pass through depending on their physical and/or chemical properties. Membrane processes are divided according to the size or molar mass of the separated substances and these include microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and Nano-filtration (NF) membranes respectively. In all these processes, the driving force is the pressure, which is different on each side of the membrane. The value of this pressure and the mechanism of transporting the particles being separated can be different, and this can complicate the scope of the particular process (Kowalik-Klimczak and Gieryoz, 2014, Cassano et al., 2001, Cassano et al., 1997, Sagle and Freeman, 2004, Ulbricht, 2006, Tasselli, 2015)

Table 3. Membrane processes(Kowalik-Klimczak and Gieryoz, 2014)

Microfiltration	Ultrafiltration	Nano filtration	Reverse osmosis
Low transmembrane pressure (<2 bar)	Low transmembrane pressure (1–10 bar)	Transmembrane pressure (5–30 bar)	Transmembrane pressure (10–100 bar)
Osmotic pressure (can be omitted)	Osmotic pressure (can be omitted)	Osmotic pressure (plays a role)	High osmotic pressure (5–25 bar)
Symmetric, porous membrane	Symmetric or asymmetric, porous membrane	Nano–porous, asymmetric membrane – integral or composite	Solid, asymmetric membrane – integral or composite
Pore size approx. 0.1–10 μm	Pore size approx. 0.001–10 μm	Pore size approx. 2 nm	Pore size < 2 nm
The mechanism of separation – sieving	The mechanism of separation – sieving	The mechanism of separation based on dissolution and diffusion	The mechanism of separation based on dissolution and diffusion

Membranes are further classified in the following way:

- Membrane materials. Organic polymers, inorganic materials (oxides, ceramics, metals), mixed matrix or composite materials.
- Membrane cross-section. Isotropic (symmetric), integrally anisotropic (asymmetric), bi- or multilayer, thin-layer or mixed matrix composite.
- Preparation method. Phase separation (phase inversion) of polymers, sol–gel process, interface reaction, stretching, extrusion, track-etching, and micro-fabrication.
- Membrane shape. Flat-sheet, hollow fibre, hollow capsule (Ulbricht, 2006, Pinnau and Freeman, 2000, Scott and Hughes, 2012, Mulder, 2012, Tylkowski and Tsibranska, 2015, Van der Bruggen et al., 2003)

Membranes for pressure-driven molecule-selective filtrations (UF, NF, RO, GS) have an anisotropic cross-section structure that is either integral or composite, with a thin (approx. 50 nm to a few micrometres) mesoporous, microporous or nonporous selective layer on top of a macro-porous support (100–300 mm thick) providing sufficient mechanical stability. By this means, the resistance of the barrier layer is minimized, thus ensuring a high membrane permeability. Macro-porous membranes with an isotropic cross-section (100–300 mm thick) are typical materials for MF, but become also increasingly relevant as base materials for composite membranes. For niche applications, track-etched polymer membranes (8–35 mm thick) with well-defined cylindrical pores of even size (between approx. 20 nm and a few micrometres) are also available (Mulder, 2012, Ulbricht, 2006)

1.3.1 Preparation techniques of membranes

Thus far from literature most of the technically used membranes (including support membranes for composite GS, RO, NF and PV membranes) are made from organic polymers and via phase separation (PS) methods (Tasselli, 2015, Ulbricht, 2006, Tylkowski and Tsibranska, 2015, Guillen et al., 2011, Rozelle et al., 2000). This is because phase inversion is the most versatile technique with which to prepare polymeric membranes. Phase inversion is a process whereby a polymer is transformed in a controlled way from a solution state to a solid state. The concept of phase inversion includes a number of diverse techniques such as precipitation by controlled evaporation, thermal precipitation from the vapour phase and immersion precipitation. A variety of morphologies can be obtained that are suitable for different applications, from microfiltration membranes with very porous structures, to more dense reverse osmosis membranes, to gas separation and pervaporation membranes, with a complete defect-free structure (Rozelle et al., 2000, Kesting, 1985, Pinnau and Freeman, 2000, Strathmann and Kock, 1977). Some of the frequently techniques used in the preparation of membranes used in different separation processes are seen in Table 4.

Table 4. Frequently used preparation techniques for separation membranes (Rozelle et al., 2000)

Process	Technique
Microfiltration	Phase inversion, stretching, track etching
Ultrafiltration	Phase inversion
Nano filtration	Phase inversion, interfacial polymerisation
Reverse osmosis	Phase inversion, interfacial polymerisation

1.3.2 Advantages of membrane based separation processes

The main advantage of a membrane based process is that concentration and separation are achieved without a change of phase and without use of additional chemicals or thermal energy, thus making the process energy-efficient and ideally suited for recovery applications. They are also characterized by low power consumption and allow for separation in a continuous manner, which can easily be combined with other unit processes and other advantages as shown in table 5 (Kowalik-Klimczak and Gieryoz, 2014, Lofrano et al., 2013, Cassano et al., 2001, Ulbricht, 2006).

Table 5. Advantages and disadvantages of membrane technology

Advantages	Disadvantages
Applicable to a wide range of processes	Selection of compatible membrane essential
Physical process with few moving parts	Generally low selectivity
Simple connections and utility requirements	Membrane fouling is a common problem
Can operate continuously or on demand	Membrane life is finite and may be short
Often no additives required	Capital investment appears high
Product can be recovered in unchanged form	Some effluents are not suitable for conventional membrane separation technology e.g. high fouling liquids
System may be scaled up or down easily and integrated with other treatment processes	
Membrane properties can be varied	
Can be used for single or multi-stage separation	
Permeate quality often independent of feed stream concentrations	
Physical disinfection performed automatically	

1.4 Membrane technology in tannery wastewater management

A number of studies have reported the implementation of membrane technology for the treatment of tannery wastewater, obtained from different production streams. The usage of various types of membranes have been reported in literature, all showing satisfactory results as compared to conventional tannery water treatment methods. The treatment of tannery wastewater using membranes has been shown to be feasible as well as cost effective when carried out on a large scale. Several studies showed that crossflow microfiltration (MF), ultrafiltration (UF), Nano filtration (NF), reverse osmosis (RO) and supported liquid membranes (SLMs) can be applied successfully on tannery wastewater treatment processes. These processes have been employed in many facets of water remediation ranging from desalination, recovery of chromium from spent liquors, the reuse of wastewater and chemicals of the deliming and bating liquor, the reduction of the polluting load of un-hairing and degreasing as well as the removal of salts (Velu et al., 2017, Velu et al., 2015, Vinodhini and Sudha, 2016, Rambabu and Velu, 2016, Ranganathan and Kabadgi, 2011, Rao and Singh, 2013, Scholz et al., 2005, Stoller et al., 2013, Suthanthararajan et al., 2004, Yamamoto and Muang Win, 1991, Krishnamoorthi et al., 1970, Hafez and El-Mariharawy, 2004, Jang et al., 2017). From the end of the 1990s, hybrid membrane processes have been developed with the purpose to improve performance in terms of product quality, plant compactness, environmental impact, and energy use. Examples of membrane integrated processes include multi-stages pressure-driven membrane processes (ultrafiltration (UF), microfiltration (MF), Nano filtration (NF), reverse osmosis (RO)) and pressure-driven membrane processes associated with membrane distillation (MD), electro dialysis (ED), or membrane bioreactors (MBRs) (Charcosset, 2015).

Ultrafiltration membranes have been largely investigated in the reduction of COD, BOD, TDS, chlorides, sulphates as well as in the removal of chromium from tannery wastewater. In work carried out by S Velu et al (Velu et al., 2015), the performance of the modified PES membranes using $CaCl_2$ as a primary modifier for tannery effluent treatment through ultrafiltration process was investigated. The membranes were prepared through the immersion precipitation method by varying the compositions. From the treatment using the modified membrane, it was found that 92–94% separation was achieved with maximum removal of BOD, COD and TDS. It was also found that blending of PES membranes with PEG and $CaCl_2$ produced membranes with modified features which resulted in comparatively higher permeate fluxes. Furthermore S Velu et al (Velu et al., 2017) prepared ASP-based PES ultrafiltration membranes via an immersion precipitation method by varying the weight ratios of PES:ASPs (i.e., 100:0 wt. %, 90:10 wt. %, 80:20 wt. %, 70:30 wt. %, and 60:40 wt. %) and reported a high BOD reduction of 92% for tannery wastewater in 80:20 PES:ASP membranes. Also ASPs fairly proved and significantly favourable for the reduction of COD, BOD, TDS, chlorides, and sulphates from both the tannery wastewater in PES membrane. The performance of the modified CA membrane for tannery effluent treatment through ultrafiltration was investigated by K Rambabu et al (Rambabu et al., 2017). The membrane surfaces incorporated with $MnCl_2$ possessed enhanced porosity and water permeability. The applicability of the membranes for industrial waste water treatment in terms of tannery effluent was also investigated. Ultra-filtration performance of tannery effluent for all the CA/$MnCl_2$ membranes produced acceptable results as per standards.

A restrictive factor for the reuse and recycling of treated tannery wastewater for irrigation and other uses is the high salt content, which usually persists even after conventional treatment. Reverse osmosis (RO) membrane treatment has been shown to significantly reduce the salt contents of tannery effluents. However, its solitary use in tannery wastewater remediation is limited because the high organic content of tannery effluent leads to rapid scaling and biofouling of RO membranes with a consequent reduction in flux rates and performance (Stoller et al., 2013, Ranganathan and Kabadgi, 2011, Scholz et al., 2005, Hafez and El-Mariharawy, 2004). The technical feasibility of the combination of reverse osmosis with conventional treatment was also reported on by K Ranganathan et al (Ranganathan and Kabadgi, 2011). In this work reverse osmosis was used as a secondary treatment method in combination with conventional tannery treatment methods. Here, higher organic load in the effluents were firstly reduced before feeding into the RO system to avoid scale formation and bio-fouling of the membranes using conventional methods. The studied tanneries showed that the removal of total dissolved solids, sodium and chloride are in the range of 91-99%. Seventy to eighty five percentage of wastewater was recovered and could be reused in the industrial operations. Azza Hafez (Hafez and El-Mariharawy, 2004) reported the use of a two phase RO treatment to remove chromium from spent tannery waters. It was found that the treatment was successful and the chromium content of the water fell within the national disposal limits.

The use of Nano filtration has also been reported in tannery wastewater remediation. Nowadays, NF membranes are widely applied to water and wastewater treatment for the removal of divalent and multivalent ions and for partial elimination of the monovalent ones. It is reported that, the larger the ratio of chromium to the COD concentration in the tannery wastewater (i.e., the less it contains organic substances), the more concentrated is solution of chromium that can be obtained in the Nano filtration process. This means it is necessary to reduce the concentration of organic substances, prior to the introduction of tannery wastewater into the Nano filtration process (stoller, 2017, Stoller et al., 2013, Galiana-Aleixandre et al., 2005, Ortega et al., 2005, Dasgupta et al., 2015) . In a review on chromium recovery methods using membranes by it is proposed that a pre-treatment of the wastewater using microfiltration and/or ultrafiltration to remove the suspension, COD, organic nitrogen, and fats from tannery effluents be conducted so as enhance the performance of the Nano-filtration membranes(stoller, 2017). The use of Nano filtration in combination with ultrafiltration has also been reported as feasible in the treatment of liming effluent as shown in wok by C Das et al (Das et al., 2007b). A significant reduction in the values of BOD, COD, TDS as well as sulphates as reported. NF is a membrane technique that can be applied to sulphate separation from wastewater (Galiana-Aleixandre et al., 2005, Taleb-Ahmed et al., 2005). The separation of charged compounds occurs due to both steric hindrance and electrostatic interactions. In work carried out by it was established that related to NF retentions in membrane experiments, it can be commented that chromium and sulphate rejections were almost constant (around 99 and 97%, respectively). The high rejections were attributed to the size exclusion mechanism separation since at the working pH there were no charge interactions. Coagulation–Nano filtration based integrated treatment scheme were employed in the study to maximize the removal of toxic Cr (VI) species from tannery effluents (Dasgupta et al., 2015). The hybrid process demonstrated a favourable and high chromium (VI) removal efficiency of over 98%.

Treatment of tannery effluent by microfiltration membranes has been, until recently, the subject of few studies and research, however, it does seem technically feasible (El Khalfaouy et al., 2017, Bhattacharya et al., 2013, Bhattacharya et al.). Most literature reports the use of ceramic based membranes in the treatment of tanner wastewater. In work by P Bhattacharya et al(Bhattacharya et al., 2013), the performance evaluation of an indigenously developed ceramic membrane from a clay–alumina mixture was evaluated toward microfiltration treatment of tannery effluent from a secondary clarifier. The study was aimed at observing the reuse efficiency of the membrane treated effluent using Pistia sp. as plant model and Poecilia sp. as fish model. About 70–86% chemical oxygen demand removal and 85% total organic carbon removal was achieved in the ceramic membrane based microfiltration process. The overall process demonstrated that microfiltration by ceramic membranes might prove as effective means of wastewater reuse for aquaculture, agriculture, as well as in industrial sectors. The efficacy, and applicability of the microfiltration treatment utilizing a local clay tubular membrane was investigated by. A treatment of industrial tannery effluent loaded by Fats, dyes and heavy metals was carried out (El Khalfaouy et al., 2017). The physicochemical characterization of the sample before and after treatment showed a remarkable increase in removal rate from 60 min to 180 min of filtration; 54.8% after one hour and 73.28% after 3 hours for COD, 73.28% after 3 hours for BOD, 26.48% after 3 hours of filtration for conductivity and a total elimination rate of Turbidity that was achieved 99% after 3 hours of treatment.

The combination of membranes technology with biological reactors has also been reported in literature. Membranes when coupled with bioprocesses are often used as a replacement for sedimentation (Stephenson et al., 2000, Munz et al., 2007, Ng et al., 2013, Wang, 2015, Suganthi et al., 2013, Fettig et al., 2017, Giacobbo et al., 2015, Lin et al., 2012). W G Scholz (Scholz et al., 2005) reported on the use of a combined MBR and RO treatment process to treat tannery effluents to an acceptable level for irrigation purposes. This treatment reduced the COD, BOD, and ammonia concentrations of the effluent by 90−100%. The MBR was shown to be an excellent pre-treatment prior to RO technology, due to the high removal efficiency of organic compounds and suspended solids, with average concentrations of 344 $mg \cdot L^{-1}$ COD and 20 $mg \cdot L^{-1}$ BOD achieved in the permeate. RO treatment reduced the salt content of the MBR permeate by up to 97.1%. J Fettig et al (Fettig et al., 2017) found that average removal efficiency for organic substances in the MBR was 81% while total nitrogen could only be removed by 36%. The combination of MBRs with an adsorption process for enhanced removal of refractory organic matter from tannery wastewater has been investigated (Munz et al., 2007) by adding powdered activated carbon to the bioreactor. In this study, small improvements in COD removal were observed, although the main purpose was to improve fouling control and achieve a better filtration performance.

1.5 Conclusion

To overcome the drawbacks associated with conventional treatment processes scientists are constantly trying to reach for newer and cleaner technologies. Membrane processes gain importance in this regard. Literature shows that pressure-driven membrane operations, integrated into some phases of the tanning process are technically feasible, reduce the environmental impact; simplify the wastewater treatment processes; permit easy reuse of sludge; reduce disposal costs; and result in a saving of chemicals and water. Their use in the previous years has been limited mainly because of high initial capital investment cost but as a result of constant developments in technology and industrialisation this phenomenon has become a thing of the past and there has been a marked rise in the use of membranes for industrial waste water remediation.

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