INTRODUCTION

Tannery industry is the significant contributor to the economy and provides large scale employment opportunity for people of economically weaker part of the society. Tanning involves a complex combination of mechanical and chemical processes. The preservation and processing of raw hides and skins for tanning process creates severe pollution problem towards environment and mankind, rather than being important from economic and employment point of view (Aravindhan et al., 2004). Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying, high-strength wastewaters. Variability of tannery wastewaters are not only from the fill and draw type operation associated with tanning processes, but also from the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product. Tanning industry
also has one of the highest toxic intensity per unit of output (Khan et al., 1999).

It discharges many toxic pollutants like sulfides, phenolic compounds, chromium and other mineral salts, dyes and solvents. Chromium contributes a major share to the hazardous nature of tannery effluent. Colored industrial effluent is the most obvious indicator of water pollution and the discharge of highly colored synthetic dye effluents is aesthetically displeasing and cause considerable damage to the aquatic life (Tripathi et al., 2011). It reduces light penetration and photosynthesis and also some of the dyes are toxic or mutagenic, carcinogenic and allergenic (Aksu et al., 2006; Kumar et al., 2006).

However, a few microorganisms such as Chaetomium globosum, Chaetomium cupreum, Fusarium solani, Aspergillus niger and Trichoderma viridae degrade tannins and utilize their carbon source. Species of Rhizobium, Pseudomonas putida and Pseudomonas solanacearum grow luxuriantly when cultured in tannin medium. (Mahadevan et al., 1985).

Problem of waste disposal can be greatly minimized if recovery of useful byproducts is made to the maximum possible extent. Numerous physical and chemical methods such as screening, flow equalization, primary sedimentation, chemical flocculation, aerobic activated sludge treatment, secondary sedimentation have been employed for the disposal of wastes. The most reliable way seems to be the biological treatment in which microorganisms serve as an efficient detoxifiers of pollutants. It is cost effective and therefore highly suitable for reduction of pollutant load of an effluent as microorganisms are capable of oxidizing the organic and inorganic constituents.

The principle of the biological treatment is based on the degradation of organic compounds and metals present in the effluent by micro-organisms (aerobic and / or anaerobic). Those microorganisms exert, on the other hand, a physical effect of organic pollution retention by gathering it in films or flakes. In bibliography, the treatment of tannery effluent by bacteria Thiobacillus ferrooxidans, Staphylococcus aureus and Vibrio sp. allows a COD removal of 69%, 80%, and 87.5% and for the disposal of CrT (caries risk test) bacteria Pseudomonas aeruginosa, Acinetobacter sp. and Hirsutella sp. give an elimination of 87%, 90% and 70%, respectively (Rajasimman et al., 2007).

This review discussed and indicated the information which had been studied experimentally. Various effluents that are produced by tannery industry can be treated by chemical, physical and biological treatment. These physicochemical methods are very expensive than biological treatment method.

**Characteristics of tannery wastewater**

The chemical composition of untreated hide or skin waste (trimmings, fleshings, splits) depends mainly on a kind of raw materials, treatment type and a process condition. The main components are protein and fats up to 10.5 % (w/w) for both groups. Moisture content is up to 60% and these wastes contain small amount of 2-6% (w/w) of mineral substances. The tanned leather wastes are mainly useless trimmings, shavings and splits. The waste groups differ mostly in size and shapes. Their chemical composition is comparable to each other. They contain 3-6% (w/w) fats, and about 15% minerals, including 3.5-4.5% (w/w) chromium (Fela et al., 2011).

The characteristics of tannery wastewater vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for a specific process, amount of water used and type of the final product produced by a tannery. Tannery wastewater is characterized mainly by measurements of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS) and Total Dissolved Solids (TDS), chromium and sulfides etc.

In general, tannery wastewaters are basic, have a dark brown colour and have a high content of organic substances that vary according to the chemicals used (Kongjao et al., 2008). The tannery wastewater is characterized by substantial organic matter content and high SS content, resulting in an average total COD concentration of 6200 mg L\(^{-1}\) and a SS concentration of 5300 mg L\(^{-1}\). Very high salinity was reflected by an average TDS concentration of 37, 000 mg L\(^{-1}\). Total Kjeldahl Nitrogen (TKN), N-NH\(_3\) and PO\(_4^{3-}\) averaged 273, 153 and 21 mg L\(^{-1}\), respectively. Tannery wastewaters are basic and their high organic content can cause considerable environmental pollution (Leta et al., 2004).

The pH values of tannery wastewaters range from 7.5 to 10 (Kongjao et al., 2008; Leta et al., 2004). The influents were characterised by high alkalinity content with a resulting pH value of above 8 due to the chemicals used in leather processing. Influent like total nitrogen and COD concentrations ranged from 927 to 2140 mg L\(^{-1}\) and
9583 to 13515 mg L$^{-1}$, respectively, whereas influent ammonium N varied from 149 to 178 mg L$^{-1}$. Sulfide and total chromium concentrations were in the range of 466.3-794 and 23.3-42.5 mg L$^{-1}$ respectively, during the process feeding stages.

It is also observed that tannery effluents are rich in nitrogen, especially organic nitrogen, but very poor in phosphorus. In addition to organic and nitrogen compounds, tannery wastewaters contain sulfide, chromium, which impart high antibacterial activity (Wiemann et al., 1998; Wiegant et al., 1999).

Most commonly used chemicals are FeCl$_3$, alums, and TiO$_2$ as coagulants, MgSO$_4$ and NiSO$_4$ as oxidizing agent, FeSO$_4$ and H$_2$O$_2$ in Fenton-photo process for COD, Cr and other cations removal. The removal efficiency of COD, total organic carbon (TOC), ammonia and sulfate using TiO$_2$/UV oxidation technique at pH 7 were found to be 3%, 8.5%, 10% and 6%, respectively indicating lower efficiencies .The results of the study illustrated that 150 mg/L coagulant (FeCl$_3$) dose in the pH range of 6.5–7.5 has shown the maximum pollutants removal capacity from the tannery effluents (Manjushree et al., 2013).

**Biological treatment of tannery wastewater**

Biological treatment of wastewater is more favorable and cost effective as compared to other physicochemical methods. Various microorganisms are capable of reducing the content of pollutants significantly by utilizing them as energy and nutrient source in the presence or absence of oxygen (Eddy, 2003).

Treatment of wastes with bacteria involves the stabilization of waste by decomposing them into harmless inorganic solids either by aerobic or anaerobic process. In aerobic process, the decomposition rate is more rapid than the anaerobic process and it is not accompanied by unpleasant odours, whereas in anaerobic process, longer detention period is required and gives unpleasant odours.

**Aerobic biological treatment**

Biodegradation of tannery wastewater using activated sludge process has been reported by many research workers (Jawahar et al., 1998; Murugesan and Elangoan, 1994; Eckenfelder, 2002; Tare et al., 2003). The performance of activated sludge process is affected by many factors. Various parameters of importance relating to growth of microorganisms and substrate utilization on which the operation of the reactor is based include mean cell residence time, Mixed Liquor Volatile Suspended Solids (MLVSS) concentration, hydraulic detention time, i.e., aeration time, food to microorganism (F:M) ratio and the dissolved oxygen in the reactor. All these studies indicate a BOD removal of 90 to 97% for the tannery effluent concluding activated sludge process as highly useful for the purpose.

A Common Effluent Treatment Plant (CETP) based on activated sludge process was employed for the treatment of tannery effluent. A significant reduction in COD and BOD levels were achieved during the course of treatment in CETP. A reduction of 98.46, 87.5 and 96.15% in bacterial counts especially in pathogens like *Escherichia coli*, *Vibrio sp.* and *Pseudomonas* sp. were observed after treatment. Pathogens were not detected in the dried sludge. Complete elimination of fecal streptococci was observed in treated effluent. Around 10.8% of microbial isolates from the effluent showed ability to reduce chromate >90%. In the treated effluent, chromium level was 5.48 mg L$^{-1}$, which exceeds the statutory limit (Ramteke et al., 2010).

Salt tolerant microbes can adapt to these saline conditions and degrade the organics in saline wastewater. Tannery saline wastewater obtained from a Common Effluent Treatment Plant (CETP) near Chennai (Southern India) was treated with pure and mixed salinity of tannery wastewater makes it difficult to be treated by conventional biological consortia of four salt tolerant bacterial strains viz., *Pseudomonas aeruginosa*, *Bacillus flexus*, *Exiguobacterium homiense* and *Staphylococcus aureus* which were isolated from marine and tannery saline wastewater samples. Experiments with optimized conditions and varying salt content (between 2 and 10% (w/v)) were conducted. Salt inhibition effects on COD removal rate were noted. Comparative analysis was made by treating the tannery saline wastewater with activated sludge obtained from CETP and with natural habitat microbes were present in raw tannery saline wastewater. Salt tolerant bacteria mixed consortia showed appreciable biodegradation at all the saline concentrations (2, 4, 6, 8 and 10% w/v) and with 80% COD reduction in particular at 8% salinity level. The consortia could be used as suitable working cultures for tannery saline wastewater (Sivaparaksam et al., 2008).

The COD removal results for tannery saline waste stream by natural habitat strains as well as activated tannery sludge proved that they were not suitable and that specialized consortia (salt tolerant) were needed for
efficient treatment. The identified salt tolerant bacterial consortia is considered as a suitable working culture for efficient biodegradation of tannery saline wastewater. A study on the biological nitrogen removal from tannery wastewater without a preliminary chemical-physical phase or an external carbon source for denitrification were carried out by Szpyrkowicz et al. (1991). They reported the removal of nitrogen by biological means from wastewaters consisting of up to 90% chrome tannery and 10% domestic sewages. The COD utilization coefficient was 12.5 mg COD for 1 mg of denitrified N. No inhibition of the process was induced by Cr or by S\(^2\)\(^-\) present in the raw wastewaters. A negative effect on the denitrification rate resulted from a high ratio between the quantity of oxygen returned with the mixed liquor and the inlet COD.

The changes in salinity appeared to affect the removal of organic matter more than the changes in hydraulic retention time or organic loading rate. Despite the variations in the characteristics of the soak liquor, the reactor achieved proper removal of organic matter, once the acclimation of the microorganisms was achieved. Optimum removal efficiencies of 95, 93, 96 and 92% on COD, PO\(_4^{3-}\), TKN and SS, respectively, were achieved with a HRT of 5 days, an organic loading rate of 0.6 kg COD/m\(^3\)/d and 34 g NaCl/L. The organisms responsible for nitrogen removal appeared to be the most sensitive to the modifications of these parameters (Lefebvre et al., 2005).

The feasibility of treating tannery wastewater containing chromium, an inhibiting compound, was studied by Farabegoli et al. (2004). The maximum chromium concentration tolerated by microorganisms is determined through aerobic and anoxic batch experiments and the biomass inhibition process is analyzed in a lab scale sequential batch reactor at higher chromium concentrations. It was observed that the chromium addition had less influence on the denitrification bacteria than on the nitrification bacteria. In addition, it was observed that nitrification and denitrification rates, at the same chromium concentration, were higher in the SBR reactor than in batch experiments with unacclimated biomass. Experimental results confirm that sequencing batch reactors are able to produce a more resistant biomass, which acclimates quickly to inhibiting conditions. SBR coupled with respirometry is a cost-effective and a clear alternative to the conventional biological system for the treatment of tannery wastewater (Ganesh et al., 2006).

**Anaerobic biological treatment**

Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and large amount of biogas (methane and carbon dioxide). Methanogenic bacteria are inhibited by sulfide, whereas acidifying and sulfate reducing bacteria do not inhibit. Three inhibiting effects of sulfide or sulfate reduction are known: direct toxicity of sulfide, substrate competition between sulfate reducing and methanogenic bacteria and precipitation of trace elements by sulfide. The extent of these effects depends on the experimental system used.

The combined anaerobic/aerobic treatment system is a long-term study and was conducted to identify the process of biological sulfate reduction in anaerobic two-stage pilot plants treating tannery wastewater. Influence of quality and quantity of wastewater on sulfate removal in both stages of the pilot plant was simultaneously tested. In the first stage, desulfurization increased with higher feed flow but the desulfurization then decreased in the second stage. The concentration of sulfate in the influent had a significant influence on the desulfurization in both stages of the pilot plants. The removal of sulfate in the first stage was approximately 30%, whereas in the second stage the desulfurization decreased with higher concentrations of sulfate in the influent. Operational parameters were adjusted in order to restrict the biological sulfate reduction to the first stage. Compared to pH 5 or 6 in the influent, biological sulfate reduction in the first stage was increased most at a pH of 7. No significant influence on COD removal or volume of gas was observed. Three pilot plants were operated in parallel to each other but no significant difference in desulfurization was noticed (Genschow et al., 1996).

Rajasimman et al. (2007) studied the performance of a single UASB reactor for treating both the solid (generated from fleshing) and liquid wastes. In this study, UASB reactor was operated at different organic loading rates ranging from 5-12 kg/m\(^3\)/d. From the results, it was observed that the COD removal efficiency of 46-85% and BOD removal efficiency of 65-93% were achieved. The gas production was in the range of 2-15 L for the given organic load.

In a continuous fixed film reactor, pretreatment of wastewater for reducing the tannin, chromium and sulfide levels gives better results in COD removal efficiency (Wiemann et al., 1998). In anaerobic up flow contact filter, COD removal efficiency was in the range of 79-95% after pretreatment compared to 60-86% for untreated.
The biogas production was in the range of 95-198 mL/hr after pretreatment compared to 98-200 mL/hr for untreated wastewater. In batch process, 60 mg/L of sulfide, 60 mg/L chromium and 400 mg/L of tannin inhibited microbial growth whereas in continuous process, toxicity occurs at higher range (Vijayaraghavan et al., 1997). In up flow fixed biofilm reactor, 60-75% COD removal and 0.36 m³/kg COD removed methane yield has been obtained. It has been found that porous polyurethane foam material is more suitable than Raschig rings as a micro carrier in fixed film reactor (Song et al., 2003).

Up flow anaerobic sludge blanket reactor with activated sludge reactor without recirculation of the sludge gave 96% COD removal at 8 days of hydraulic retention time and 71 g/L of total dissolved solids (Lefebvre et al., 2005). In up flow anaerobic sludge blanket reactor, average COD removal efficiency was 65% at organic loading rate in the range of 0.2 - 7 kg/m³.d⁻¹. The average gas production is 0.3 m³/kg of COD removed (Suthanthararajan et al., 2005). A combined aerobic and anaerobic treatment of tannery with 900 mg/L dissolved organic carbon corresponding to discharge of 23 kg/ton of raw hides gave 85% removal efficiency of the dissolved organic carbon (Reemtsma et al., 1997).

Decolorization of tannery effluents

Biological systems are recognised by their capacity to reduce biochemical oxygen demand (BOD) and chemical oxygen demand (COD) through conventional aerobic biodegradation (Kornaros and Lyberatos, 2006; Balan and Monteiro, 2001). On the other hand, in recent years, there is a tendency to use biological treatment systems to treat dye-bearing wastewater. Some species of bacteria are capable of dye decolorization, either in pure cultures or in consortia have been reported. The utilization of microbial consortia offers considerable advantages over the use of pure cultures in the degradation of synthetic dyes (Jadhav et al., 2010).

A. Using individual Bacillus species isolated from effluent: The culture under agitation conditions demonstrated a better growth than that under static conditions. This study reviews that the bacterial species Bacillus exhibited dye decolorizing activity only when incubated under the stationary conditions, whereas, negligible decolorization can be seen under the agitating conditions. Stationary cultures exhibited apparently complete decolorization of effluent within 96 hrs of incubation and further incubation did not improve decolorization (Kornaros and Lyberatos, 2006). Anaerobic or static conditions were necessary for bacterial decolorization through the cell growth. Under aerobic conditions, azo dyes are generally resistant to attack by bacteria. Azo dye decolorization by bacterial species if often initiated by enzymatic reduction of azo bonds, the presence of oxygen normally inhibits the azo bond reduction activity since aerobic respiration may dominate utilization of NADH; thus impeding the electron transfer from NADH to azo bonds (Ilanjiam et al., 2011).

B. Using microbial consortium: Microbial consortium prepared from strains isolated from tannery effluent and sludge can be used for decolorization of effluent with 1:10, 1:5, 1:2 dilutions and undiluted effluent. In 1:10 and 1:5 diluted effluents, complete decolorization took place after 10 days and 30 days while no decolorization took place in 1:2 diluted and undiluted effluents after 30 days. Lower decolorization efficiency is due to higher inhibition at high dyestuff concentration (Bakshi et al., 2006). This indicates that as the concentration of dye in effluent increased, the rate of decolorization was decreased.

C. Using consortium comprising of algae and bacteria: Consortium comprising of algae and bacteria can show complete decolorization of 1:10 diluted effluent within 3 days. Here rate of decolorization was faster as compared to individual algae and bacteria. Consortium comprising of algae and bacteria as the most efficient for decolorization of effluent followed by single bacterial isolates and microbial consortium followed by algae. This indicates that consortium comprising of bacteria and algae could be good alternatives to the conventional treatment methods for decolorization and removal of chromium from leather and other industrial effluents.

Combination of biological methods with physical/chemical methods

Degradation of leather industry wastewater by aerobic treatment incorporating Thiobacillus ferrooxidans, Fenton's reagents and combined treatment was studied by Mandal et al. (2010). The sole treatment by Fenton's oxidation involving the introduction of 6 g FeSO₄ and 266 g H₂O₂ in a liter of wastewater at pH of 3.5 and 30°C for 30 min at batch conditions reduced COD, BOD, sulfide, total chromium and color up to 69, 72, 88, 5,
100% and *Thiobacillus ferrooxidans* alone showed maximum reduction to an extent of 77, 80, 85, 52, 89 respectively in 21 day treatment at pH 2.5, FeSO₄-16 g L⁻¹ and temperature of 30°C.

The combined treatment at batch conditions involving 30 min chemical treatment by Fenton's oxidation followed by 72 h biochemical treatment by *Thiobacillus ferrooxidans* at batch conditions gave rise up to 93, 98, 72, 62 and 100% removal efficiencies of COD, BOD, sulfide, chromium and color at pH of 2.5 and 30°C. They observed a decrease in photo absorption of the Fenton's reagent treated samples, as compared to the blanks, at 280, 350 and 470 nm wavelengths. This may be the key factor for stimulating the biodegradation by *Thiobacillus ferrooxidans*.

Seawater-induced flocculation of alkaline tannery wastewater can increase the removal efficiency of organic compounds, such as particulate, colloids, colored compound and other dissolved organic compounds. Flocculation through the use of seawater was used as the primary treatment in the onsite tannery wastewater treatment plant. Evaluation of the potential biological treatment was performed by the activated sludge system of suspended microorganisms using seawater flocculated tannery wastewater. The pH adjustment of the influent wastewater and PO₄-P addition after seawater flocculation were the most important operational parameters to enhance the removal efficiency of COD in the activated sludge process. Removal efficiency of COD increased with increase in sludge retention time (SRT). With the pH adjustment and PO₄-P addition after seawater flocculation, 75% of COD was removed at the SRT of 15 days. Experimental results demonstrated that seawater flocculation was more effective than the comparable ferric salt flocculation in enhancing the biological treatment during the 110 days of operation (Ryu et al., 2007).

Biological degradation, carried out in a sequencing batch biofilm reactor, with chemical oxidation, performed by ozone is an innovative tannery wastewater process. Furthermore, it is proved that the combined process is characterized by a very low sludge production. The combined treatment at the laboratory scale with and without ozonation was found to be very satisfactory only in the latter instance where recorded COD, NH₄-N and TSS average removals were 97, 98 and 99.9%, respectively. In fact, the measured specific sludge production resulted unexpectedly much lower than the value reported for conventional biological systems (Di Iaconi et al., 2002).

High sulfide concentration present in treated treated wastewater may render aerobic biological treatment unsuitable. Hence, it became essential to include sulfide removal unit operation preceding aerobic biological unit. Among the techniques available oxidation of sulfide by air using activated carbon as catalyst gained importance for its removal of COD, BOD and TOC in addition to elimination of sulfide in wastewater. Anaerobic treatment of tannery wastewater in high rate close type reactors leaves sulfide in the range of 31-795, COD 395-1886, BOD 65-450 and TOC 65-605 mg L⁻¹. Thus post anaerobic treatment of wastewater was required to meet discharging standard.

The effect of S²⁻/O₂ ratio and hydraulic loading rate on removal of sulfide and organics in counter current reactor containing activated carbon were found. The percentage removal of COD, BOD, TOC and sulfide from anaerobically treated wastewater were 81, 85, 82 and 100%, respectively. The sulphate content of catalytically oxidized effluent was increased by 24% at S²⁻/O₂ ratio of 0.3353 and dissolved solids content was increased by 36% (Sekaran et al., 1996).

**DISCUSSION**

Various physicochemical techniques used for wastewater treatment can be applied to tannery wastewater (to the entire process or to individual step in the process) but these processes are expensive. Biological treatment of wastewater is more favorable and cost effective as compared to other physicochemical methods. Tannery wastewater is difficult to treat because of complex characteristics like high BOD, COD, suspended solids, sulfide and chromium. The main source of sulfide in tannery effluent is beam house operations. Anaerobic treatment of tannery wastewater gives better results but formation of sulfide in anaerobic reactors restricts its application. Various phototrophs and chemotrophs have been used for sulfide removal but requirement of light source is the major problem in case of phototrophs. Chemotrophs require careful control of oxygen to produce sulfur instead of sulfate but still some sulfide formation is there. Biological treatment methods also appear to be a better choice for the removal of color and organic content; however, some of the questions are yet to be answered on its process efficiency. This is because of the lack of information on various aspects such as desirable influent COD, optimal level of volatile fatty
acids (VFA) concentration in the reactor, the reliable estimates of the biokinetic constants and their dependence on the substrate levels. In the field of wastewater treatment, it is generally accepted that anaerobic treatment is less energy-intensive and, hence, preferable to aerobic treatment. Under aerobic condition, bacteria oxidize the organic compounds found in the wastewater for cellular growth and cell maintenance. Anaerobic treatment accomplishes more than 70% color removal while aerobic treatment which follows removes the rest by 80%. This review also indicates the ability of bacteria to convert or transform partially degraded dye products using specific enzymes into metabolic intermediates which can enter their central metabolic system and can further be used to obtain energy for cellular activities and growth of the microbes. Biological treatment module was carried out so that reduction of the chromium level of the said tannery industry wastewater in an efficient and cost effective manner could be achieved. ‘Biological Treatment’ shows a remarkable reduction in the chromium values up to 51% and it shows little inhibitory effects due to the presence of other heavy metals with the chromium effluent. In the Chemical Treatment phase, a reduction of chromium values up to 10% and 88% respectively has been obtained. Moreover, this chemical treatment is cost effective and very low amount of dose is required. So, in this case the application of combined process of physical or chemical with biological process to treat tannery wastewater would give satisfactory results compared to individual treatment process.

CONCLUSION

Tannery wastewater is difficult to treat because of complex characteristics like high BOD, COD, suspended solids, sulfide and chromium. This review examines the extent of pollution created by tanneries and the different biological processes available for the treatment and disposal of tannery wastewater. Biological treatment methods appear to be a better choice for the removal of color, organic content, suspended substances, sulphur, chromium etc. This review also tried to accumulate the research output that indicated the anaerobic treatment is superior in most respects for the treatment of tannery wastewater. The biological treatment of tannery effluents is more favorable and cost effective than the other processes. But, when the effluents are non-biodegradable, then physical/chemical processes combined with biological process is the better option for the treatment of tannery effluents.

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