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**BIOLOGICAL EFFLUENT TREATMENT METHODS OF TANNERY WASTE
WATER – A REVIEW**

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Abstract: Manufacturing of leather products produced numerous by products, solid wastes, high amount of waste water containing different loads of pollutants and increases health risks for human beings and environmental pollution. Moreover, the process economy is as important as removal efficiency during the process evaluation task. The treatment of tannery effluent is a complex technological challenge because of the presence of high concentrations of organic and inorganic pollutants of both conservative and non-conservative nature. In this review paper information relevant to tannery effluents and its prospective on biological treatment processes and other recent potential biological processes are discussed. Emphasis is laid on the removal of organic matter (COD/BOD), NH₄-N and sulphide/sulphate from tannery effluent. Though the aerobic process is efficient in treating tannery effluent, it requires an extended aeration time at low organic loading rates and thereby increasing the overall treatment cost. Anaerobic process is not effective because of sulphide inhibition problems. Sulphide inhibition control is essential for successful anaerobic treatment of tannery effluent. Sequencing Batch Reactor (SBR) and membrane reactor technologies are found to be effective for removal of organic matter and ammonia, but they are having very high operational cost. The recent development shows possibility of high rate treatment of tannery effluent in an alternate and an effective way suitable to both developing and developed countries. This article discusses the review of few tannery treatment methods in waste water. Thus; the paper

covers various advanced methods of effluent treatments from physical, chemical, to biological or combination of these methods. From this review it shows that the combination methods give satisfactory results compared to other types of effluent treatment processes.

Keyword: SBR, Tannery Waste Water, COD, BOD, Solid Waste, Sulphidogenesis; Anoxic ammonia removal

I. Introduction

Tanning is one of the oldest industries in the world. With the growth of population and the resultant increasing demand for leather and its products, large commercial industries have been established. Tannery productive cycle includes a series of chemical treatments using a large number of chemicals such as surfactants, acid and metal-organic dyes, natural or synthetic tanning agents, sulphonated oils, salts, etc. to transform animal skin into an unalterable and imputrescible product. Tanning involves a complex combination of mechanical and chemical processes. The preservation and processing of raw hides and skins for tanning process cause severe pollution problem towards environment and mankind, rather than being important from economic and employment consideration. The tanning operation in which organic or inorganic materials become more chemically bound to the available substance and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. Chrome tanning produces leather better suited for certain applications, particularly for the upper parts of boots and shoes, and requires less processing time than traditional vegetable tanning [1]. Tanneries are such industries which contributes a major part in water usage. Obviously the wastewater effluent from this unit contains considerable amounts of hazardous pollutants, and where heavy metals are very common[2]. Manufacturing of leather and leather goods produces numerous by-products, solid wastes, high amounts of wastewater containing different loads of pollutants and emissions into the air. The uncontrolled release of tannery effluents to natural water bodies increases environmental pollution and health risks. Tanning is a process of making leather from skin involves a complex combination of mechanical and chemical processes. Due to the two foremost constituents of the wastewaters, different organic ingredients being responsible for high BOD and COD values expose an immense pollution problem [3]. The tanning industry is familiar with its being a potentially pollution-intensive industry. The environmental impacts from tanneries result from liquid, solid and gaseous waste streams. It must be emphasized that 4 million tons of solid waste per year is generated by the global tannery industry. According to some estimation, about 0.8 million tons of chromium tanned shavings are generated per year globally [4].

About 55% of total leather is processed from Tamilnadu and many tannery units are spread over in Chennai, Ambur, Ranipet, Vaniyambadi, Erode, Dindigul, , and Trichy. More than 70% operating tannery industries adopt chrome tanning process and 30% adopt vegetable tanning process. Effluent Treatment Plant (ETP) is connected to the Common Effluent Treatment Plant (CETP). There are 14 operating CETPs in Tamil Nadu. The CETP at Pallavaram treats around 3000m³/day of wastewater from the tanneries and process mostly semi-finished to finished leather product. It is named as Pallavaram Tanners Industrial Effluent Treatment Co., (PTIETC). Pallavaram is an industrial area in southern part of Chennai metro and located on the Trichy-Chennai National Highway. There are almost 200 tanneries operating in and around Pallavaram area[5].

II. Statement of the environmental problem

The Leather Tannery industry is committed to reducing environmental impacts of their activities, and to continuously improve their environmental performance and to meeting or exceeding the requirements of all applicable environmental laws and regulation. The tanning industry generates solid wastes, effluents and gaseous emissions that have adverse environmental impacts. Air emissions from the tanneries to the ambient environment are not significant. However, the workers inside the tanneries are exposed to gaseous and vapor emissions particularly in the areas where

liming, de-liming and surface finishing operations are carried out. The presence of sulfides in the wastewater is the source of hydrogen sulfide emission. Ammonia gas can be also released during de-liming process reaching a level higher than TLV (25ppm) by volume. Most of private tanneries are connected to the general public sewers. The wastewater generated by the tanning industry is high in suspended organic and inorganic matter, hair, oil and grease, chromium salts and other.

III. Sequential Batch Reactor

A SBR is sort of activated sludge method applied for the wastewater treatment. According to 1999 U.S. EPA report, SBR operates based on space and ASP based on time. The operation of SBR has been described by Irvine and Davis. SBR can treat wastewater that is biodegradable, which can be directly generated from process or it can be pretreated by anaerobic digestion. To reduce organic load i.e COD and BOD the air is bubbled through wastewater and activated sludge mixture. The treated effluent could also be appropriate for discharge to water receiving bodies like river, pond, surface waters or presumably to be used towards land. There are many configurations of SBRs, the fundamental method is analogous. SBR installation may consist of one or additional tanks which is operated mainly as fully mixed reactors. The raw waste (influent) enters the one end and treated water (effluent) goes out the opposite. In multiple tank system one tank is operated as settled and decant mode while opposite in aerating and filling mode. This helps to mix the incoming influent and the returned activated sludge. High amount of pollutants like BOD, COD, TS, Total Kjeldahal Nitrogen (TKN), phosphorous, oil and grease removal have been observed in treatment of various effluents like Tannery, Paper mill, Coke oven, Distillery, Brewery, Diary, Piggery, Petrochemical, Textile, Palm oil refinery, complex chemicals, etc.

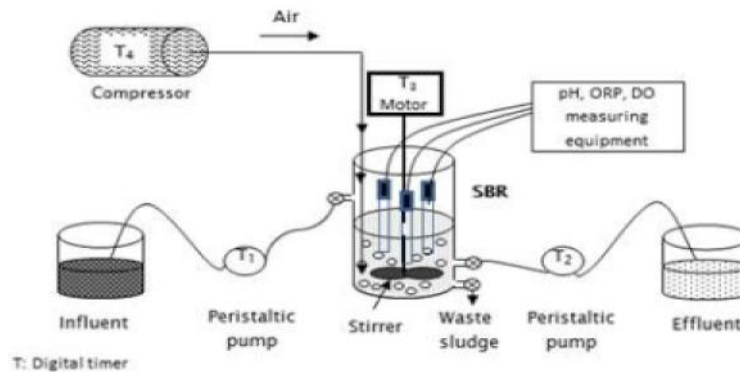


Fig.1 Schematic Diagram of SBR Process is Presented

The SBRs are used for (i) Anaerobic (ii) Aerobic treatment of wastewater which is described below.

a) Anaerobic Process

Anoxic SBR are often used for anaerobic treatment processes. During this case, the reactors are purged of oxygen by flushing with nitrogen. As the microorganisms multiply and die, the sludge at intervals in the tank increases with time which is removed using sludge pump. The mass or age of sludge in the tank is closely monitored at time intervals, because it has a vigorous impact on the treatment method. The sludge is allowed to settle till clear water is obtained at the top of the reactor as supernatant, mostly 20-30% of the tank contains sludge. The clear liquid can be further treated or it can be used as water source to vegetables.

b) Aerobic Process

When oxygen is added to the SBR, it enhances the multiplication of aerobic microorganism so that they can consume the nutrients and hydrocarbons. The method converses ammonia to chemical group and nitrate forms is referred to as nitrification. COD and BOD also reduced by oxidation bacteria. The sludge attached with microorganisms is allowed to settle in the tank. The aerobic microorganism still multiply till the dissolved oxygen is virtually spent. The schematic diagram of SBR process is presented in Figure 1. The utilization of SBR in wastewater treatment is presented in Table 1.

IV. Need For Study

Nearly 40-45m³ of waste water is generated during processing of one tone of raw skin/hide. The waste water is highly polluted in terms of biological oxygen demand(BOD), chemical oxygen demand (COD), suspended solids (SS), nitrogen, conductivity, sulphate, sulphide and chromium. The high biological oxygen demand (BOD)content of the effluent will affect the survival of gill breathing animals of the receiving water body and high COD value indicate toxic state of the wastewater along with presence of biologically resistant organic substances. The degradation of tannin may cause eutrophication. The high salinity and TDS of the effluent may result in physiologically stressful conditions for some species of aquatic organisms due to alterations in osmotic conditions. Studies show that increase in salinity causes shifts in biotic communities, limit biodiversity, exclude less tolerant species and cause acute or chronic effects at specific life stages. Changes in the ionic composition of water can also exclude some species while promoting population growth of others. The pollutants are hazardous to human and aquatic life resulting in bioaccumulation. Hence, the wastewater needs to be treated to meet the discharge standards for being let into the water bodies or reused.

V. Literature Review

Li and Zang (2002) studied the SBR performance for treating dairy wastewaters with various organic loads and HRTs. At 1 day HRT and 10000mg/l COD, the removal efficiency of COD, Total solids, Volatile solids, Total Kjeldal Nitrogen (TKN) and nitrogen was reported to be 80.2,63.4,66.3,75 and 38.3% respectively.

Uygur and Kargi (2004) experimented with four step SBR (anaerobic, oxic, anoxic, and oxic phases with HRT of (1h/3h/1h/1h) for investigation of nutrient removal from synthetic wastewater at different phenol concentrations ranging from 0 to 600mg/l. It was observed that the nutrient removal efficiency was almost 90% and 65% for nitrogen and phosphorus respectively and above 95% for COD removal for phenol concentration up to 400mg/l. The performance of SBR was drastically affected above 400mg/l concentration of phenol. There was similar observation in case of SVI as there was drastic increase from 45ml/g to 90l/g.

Catalina et al. (2011) carried evaluation of nitrogen removal in wastewater from a meat products processing company, using a SBR at pilot scale. The complete cycle of the SBR (filling, reaction, settling and draw) was 8h, with three cycles performed per day. It was concluded that the SBR was an appropriate treatment system to perform the joint removal of organic matter and ammonia nitrogen in wastewater from a meat processing company products, demonstrating the SBR system to operate with discharges that present strong variations in composition.

Kim et al. (2008) researched the treatment of low strength swine wastewater with municipal wastewater in enhanced SBR which involves eight steps of treatment i.e. fill, contact, settle, decant, nitrification, refill, react and idle. It was proved that independent nitrification can be achieved by incorporating the contact period within the system and nitrification in the external reactor. The COD, TN and TP removal were 87%, 81% and 60% respectively which can be considered far better than conventional treatments. As the ammonia nitrogen was nitrified 70% in the external reactor, this system does not require any externally added carbon for effective removal of nutrients and biodegradation of organic matter. Finally it was concluded that the system is best suited for regular as well as advanced wastewater treatment particularly for low strength wastewaters.

Nardi et al. (2011) carried the research work for advanced wastewater treatment of poultry slaughter house for its reclamation. The advanced treatment consisted of use of SBR, chemical-DAF and UV disinfection. The wastewater was given anaerobic pretreatment in the form UASB. The use of SBR was aimed denitrification. The total denitrification efficiency was more than 90%, also the TCOD removal was $54\pm 24\%$ and TP 43%. The sludge also presented good settling characteristic with SVI $118\pm 35\text{mLg}^{-1}$. Authors concluded that the SBR system along with chemical-DAF and UV disinfection is appropriate for anaerobically pretreated poultry wastewater.

VI. Effect of HRT

HRT play an important role during wastewater treatment in SBR. HRT is defined as the time required by the wastewater to pass through the system. Effect of HRT on degradation of pollutants from coking wastewater (CWW) was studied in a pilot plant SBR. Average values of COD= $1100\text{--}1700\text{mg/dm}^3$, Phenol= $185\text{--}253\text{mg/dm}^3$, thiocyanide= $210\text{--}485\text{mg/dm}^3$, ammonia nitrogen= $532\text{--}567\text{mg/dm}^3$ contained in CWW. For HRT= $58\text{--}225\text{h}$, COD removal was in between 69 to 81%, phenol removal was 97 to 99%, SCN-removal was 90 to 98%, $\text{NH}_3\text{-N}$ removal was 41 to 85%. In the study, 58h HRT was found to be optimum. A study done by Kushwaha et al. for the treatment of dairy waste water showed 96.5% COD removal and 64.61% TKN removal at HRT= 24h . Similar studies were performed by Thakur et al. to treat petroleum refinery wastewater (PRW) which had a COD= $350\pm 25\text{mg/dm}^3$ and TOC= $70\pm 10\text{mg/dm}^3$. HRT was varied in between 0.56 to 3.33 days. Among these studies, HRT= 0.83d gave maximum 80% COD and 83% TOC removal. The reason for lower COD and TOC removal at HRT >0.83 was due to lower growth rate of microorganisms and accumulation of older cell.

Maranó'n E et al.,(2008) discussed the HRT play an important role during wastewater treatment in SBR. HRT is defined as the time required by the wastewater to pass through the system. Effect of HRT on degradation of pollutants from coking wastewater (CWW) was studied in a pilot plant SBR. Average values of COD= $1100\text{--}1700\text{mg/dm}^3$, Phenol= $185\text{--}253\text{mg/dm}^3$, thiocyanide= $210\text{--}485\text{mg/dm}^3$, ammonia nitrogen= $532\text{--}567\text{mg/dm}^3$ contained in CWW. For HRT= $58\text{--}225\text{h}$, COD removal was in between 69 to 81%, phenol removal was 97 to 99%, SCN-removal was 90 to 98%, $\text{NH}_3\text{-N}$ removal was 41 to 85%. In the study, 58h HRT was found to be optimum.

Kushwaha et al.(2013) studied for the treatment of dairy waste water showed 96.5% COD removal and 64.61% TKN removal at HRT= 24h . Similar studies were performed by Thakur et al. to treat petroleum refinery wastewater (PRW) which had a COD= $350\pm 25\text{mg/dm}^3$ and TOC= $70\pm 10\text{mg/dm}^3$. HRT was varied in between 0.56 to 3.33 days. Among these studies, HRT= 0.83d gave maximum 80% COD and 83% TOC removal. The reason for lower COD and TOC removal at HRT >0.83 was due to lower growth rate of microorganisms and accumulation of older cell.

Table 1: Applications of SBR in wastewater treatment

S. No.	Wastewater	Experimental Setup/ Waste properties	Parameters observed	Result/ Conclusion	Reference
1	Wastewater from pulp and paper mill	The Laboratory scale reactor consists of four 4dm ³ capacity with the use of aquarium type air pump for aeration. Minimum of 2 mg/dm ³ of DO level were maintained. The experiments were performed at 25–30°C. Wastewater characterized as COD of 1200-1400 mg/dm ³ , BOD of 550-790 mg/dm ³ , TSS of 200-500 mg/dm ³ and pH varies from 6.2-6.6.	Effect of MLSS concentration, volume exchange rate, aeration time, temperature and cycles per day.	COD removal efficiency under the optimized condition was 93 %, at MLSS = 4500 mg/dm ³ , aeration time = 5 h per cycle, temperature = 30 °C	Tsang et al. (2007)
2	Landfill leachate.	The reactors, with a working volume of 6 dm ³ each were used. The stirrer was operated at 36 rpm. The leachate was supplied to the reactors for 4 h of the cycle at 0.125 dm ³ /h (SBR 1), 0.2 dm ³ /h (SBR 2), 0.5 dm ³ /h (SBR 3) and 0.75 dm ³ /h (SBR 4). All the four SBRs were operated at HRT of 12, 6, 3 and 2d.	COD and BOD ₅ removal efficiency and bio mass yield co-efficient was observed.	The process had little effect to BOD ₅ removal efficiency, while better COD removal efficiency.	Kulikowska et al. (2007)
3	Treatment of municipal solid wastewater	The comparison of SBR with normal working procedure (Control reactor) to the SBR using zeolite powder to increase the activity of sludge was performed. The reactors used were of 0.3m diameter and 0.6 m height with an effective volume of 31.1dm ³ . The characteristics of the wastewater used in the study was SS = 94-212 mg/dm ³ ; COD = 274-421mg/dm ³ ; NH +N=25.5-44.24 mg/dm ³ ; TN= 4 33.5-68.7 mg/dm ³ ; TP = 2.65-4.85mg/dm ³ and pH=6.67-7.86. The Zeolite concentration was maintained 1000 mg/dm ³ .	Operational efficiency of both the SBRs in removing COD, TN, NH+ N and TP. Variation of DO in operating cycle and Comparison of sludge characteristics	The addition of Zeolite powder enhanced the activity of the sludge and specific O ₂ utilization rate. The pollutants like COD, TN, NH +N ₄ and TP was removed in shorter length of time. The zeolite contained reactor treated 1.22 times more wastewater than normal SBR.	He et al. (2007)
4	Treatment of synthetic phenolic wastewater.	Two identical SBRs of working volume of 5 dm ³ were used. It was operated with fill, react, settle and draw periods in the ratio of 4:6:1:1 for a cycle time of 12h. First reactor was aerated during fill and react phase, while the second was aerated only in the react phase.	The performance of SBR was evaluated for aerated and unaerated fill phase.	The fill mode was not effective for phenol and COD reduction; The kinetic studies found to high concentration of phenol has an inhibitory effect on the degradation rate of phenol.	Chan and Lim (2007)
5	Landfill leachate	The SBR bioreactor was made of plexiglas with operating volume of 50dm ³ It was operated with the cycle time of 24h with fill phase 2h, anoxic phase 2h, aeration 18h, settling 1h, decant and idle period 1h.	Removal of COD BOD and N, Change of Alkalinity and cycle time study	Removal efficiencies of COD=93.28%, BOD = 98.76%, TN = 84.74% and NH + N=49.21%	Zhou et al. (2006)

6	Synthetic wastewater	Three identical SBRs were used in the study with anaerobic/aerobic sequence to reduce COD and phosphorus. The working volume of the reactor was 4 dm ³ with the operating cycle of 14h.	COD and phosphorus removal.	Complete removal of 20 mg/dm ³ PO ₄ -P was achieved in 35d of operation. The COD removal efficiency was 90%	Sarioglu (2005)
7	Synthetic wastewater	Four cylindrical SBR of 127 cm height and 5 cm diameter with a working volume of 2.5 dm ³ was used with 5mints for filling and 5 mints for decantation. Total operating cycle was 4h. The air flow rate was maintained to 3dm ³ /min.	Granular characteristics and sludge settleability.	Granules were successfully cultivated and settled in 5mints	Qin (2004)
8	Synthetic wastewater	The SBR was operated under different conditions. It consists of a 5 dm ³ working volume with microprocessor controlled for aeration, pH, agitation and DO. SBRs performance was done with three different operating schemes i.e. one with three step operation: anaerobic (An)/anoxic (Ax)/ oxic (Ox); four step operation: An/Ox/ Ax/Ox and five step operation: An/Ax/Ox/Ax/Ox	COD,phosphat e and nitrogen removal.	The most of the COD and ammonium were removed during the first three steps. However,for removal of phosphate-P and nitrate-N five-step operation was required.	Kargi and Uygur (2003)
9	Petroleum refineries	SBR with working volume 15 dm ³ at 15°C was used. One third of the reactor was filled with inoculum. The operation cycle from fill to decant phase was 6h in which 4.3h was for react phase and the rest was distributed in other phases.	Amonical nitrogen and phenol removal.	Upto 95%, NH ⁺ and phenol removal was noted.	Silva et al. (2002)
10	Phenolic	Application of granulated activated carbon (GAC)in SBR to treat wastewater with phenolic shock loading was studied. Two reactors of 12 dm ³ and operating volume of 10dm ³ was used. The adsorbent used was lignite based granular activated carbon with 0.75 mm diameter.	Adsorption characteristics of GAC,step up shock loading, short term fluctuation and stepwise augmentation for phenol removal.	SBR with GAC was found to high stability to phenol shock loading and worked as a buffer by adsorbing the high strength of influent phenol and as a supporting media for microorganisms	Vinitnant harat et al (2001)
11	Petrochemical wastewater	The three phase experimentswere performed for study of different parameters in four reactors of glass cylinder have capacity of 3.5dm ³ . The working volume of SBRs was 2dm ³ . The flow rate of wastewater was 2dm ³ /d and 0.4dm ³ /d. The HRT was maintained to 2d and SRT to 10d.	Phenol removal at different operating parameters.	Degradation of phenol reached to less than 0.1 mg/dm ³ from 950 mg/dm ³ .	Hsu (1986)

VII. Effect of Fill Time

Yu and Gu, did fill time studies for treatment of synthetic phenolic wastewater in the two SBRs which was operated at aerated fill and un-aerated fill conditions. When phenol concentration was low (<400mg/dm³), the SBR was operated at un-aerated fill condition performed better to that SBR operated with aerated fill condition. It was also noted that at higher phenol concentration (>800mg/dm³), accumulation of phenol during fill period had became inhibitory to microorganisms causes low phenol removal efficiency and low growth of dispersed biomass. The studies show,fill

strategies should be selected according to wastewater composition, biodegradability and concentration of toxic substances in wastewater.

Thakur et al. studied the fill time variation for COD and TOC removal of PRW. In fill time of 0.5, 1 and 2h, respectively, COD removal efficiencies were 58%, 68% and 74%, and TOC removal were 28%, 51% and 59%. Pollutants removal rate was low initially for higher fill time, which was increased when time proceeded.

Kushwaha et al. revealed the effect of fill time was also performed. For fill time = 0 to 2h, they have also found increase in COD reduction with increase in fill time. DO was found to increase with increase in fill time.

Tomei et al. performed the biodegradation of 4-nitrophenol (4NP) in a SBR. In the experiments, both long feed phase and high biomass concentration showed much effective to reduce the 4NP.

Sahinkaya and Dilek investigated the biodegradation kinetics of 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) separately in batch reactors and in mixed SBR.

Fang et al. investigated removal efficiency of phenol from synthetic wastewater using anaerobic thermophilic condition (55°C). Maximum phenol removal 99% was achieved at HRT of 40h.

Sarfaraz et al. conducted anoxic treatment for degradation of phenol in SBR using granular denitrifying sludge. The different cycle lengths and influent phenol concentration was main variable parameters. In the process upto 80% phenol was degraded from its initial value of 1050 mg/dm³ at cycle length of 6h, which was corresponded to 6.4g COD/dm³.d. When phenol concentration was increased, the phenol and COD removal efficiencies was decreased. Tomei et al. performed the biodegradation of 4-nitrophenol (4NP) in a SBR. In the experiments, both long feed phase and high biomass concentration showed much effective to reduce the 4NP.

Shariati et al. have treated synthetic petroleum wastewater in a SBR at different HRT, similarly, Kutty et al. also used six different SBR to treat PRW having COD concentration in the range of 500-750 mg/dm³. Experiments were performed at anaerobic and aerobic modes with a 24h cycle in 2dm³ reactor. The process gave COD removal of 91%, 91%, and 88% respectively, for aerobic reactor, combined anaerobic-aerobic reactors and aerobic mixed.

Derlon et al. studied the formation of aerobic granular sludge in SBR for MWW treatment. Granular sludge formation was possible at low upflow velocities during anaerobic feeding phase.

Alvarez et al. studied the treatment of DS in a two stage anaerobic pilot plant technique, total COD removal of 49%-65% obtained with a 35.1% methane conversion from influent COD.

Gutiérrez et al. did the lab scale removal of carbon and nitrogen from dairy wastewater using SBR. They used a 15dm³ reactor for treatment and found the aeration time 4.5h to optimum. During operation, the HRT was 4 days and 20 days. In the process, COD reduction reached to 97% and total nitrogen to 90%.

Kushwaha et al. for treatment of dairy wastewater, the optimization of parameters like fill time, HRT, sludge disposal was done. Up to 97.05% COD removal and 63.08% TKN removal was observed.

Rajab et al. investigated the performance of a lab scale anaerobic/aerobic SBR for poultry slaughterhouse wastewater. The anaerobic reactor of volume 12dm^3 was used but the aerobic reactor volume varied according to the flow rate. Experiments were performed at room temperature of $26\text{-}28^\circ\text{C}$. The results obtained were overall COD removal of $97\% \pm 2\%$, $\text{NH}_3\text{-N}$ removal $98\% \pm 1.3\%$, oil and grease removal $90\% \pm 11\%$ and total suspended solids (TSS) removal $96\% \pm 3\%$.

Gonzalez et al. worked on the photo fenton oxidation and sequential batch biofilm reactor. For $200\text{mg}/\text{dm}^3$ of antibiotic sulfamethoxazole containing water, the 75.7% TOC removal obtained. Biodegradation of organic compounds Dichlorodiethyl ether (DCDE) was performed in SBR. For this, removal of organic was 92% in term of COD and 95% in term of TOC.

Miqueleto et al. analysed the performance of anaerobic SBR for COD removal of synthetic glucose solution. At optimum condition, 93-97% COD removal was seen for $500\text{mg}/\text{dm}^3$ glucose solution.

Jang et al. revealed the evaluation and characterization of granular formation was performed by aerobic and anoxic conditions. After 50 days of operation, the size of granules was found to be 1 ± 0.35 to $1.39 \pm 0.45\text{mm}$. COD removal and nitrification efficiency was 95% and 97% respectively.

Frigon et al. treated the cheesy whey wastewater sequentially in anaerobic and aerobic SBR. They found, in first 48 cycles (each cycle of 2, 3 and 4 days) with organic loading rates of 0.56, 1.04 and $0.78\text{ gCOD}/\text{dm}^3/\text{d}$, for 2, 3 and 4 days, respectively; COD removal was $89 \pm 4\%$, $97 \pm 3\%$ and $98 \pm 2\%$. Whereas, in the second 16 cycles (each cycle of 2 days) with organic loading rate $1.55\text{gCOD}/\text{dm}^3/\text{d}$, COD removal was $88 \pm 3\%$.

Lin et al. revealed the high strength semiconductor wastewater using fenton oxidation was performed in SBR. In the process 95% COD and 99% color removal was seen after fenton oxidation with a $5\text{g}/\text{dm}^3$ FeSO_4 dosage and $45\text{g}/\text{dm}^3$ H_2O_2 concentration and 180min of digestion.

VIII. Biological Method

Bioremediation is a process that uses naturally occurring microorganisms to remove or neutralize pollutants in to less toxic substances. Microbes are the significant sustainable agents for the detoxification and degradation of industrial pollutants. Microbes decompose waste into harmless inorganic solids by anaerobic or aerobic process. In anaerobic process, longer detention period is required and gives unpleasant odours whereas aerobic process does not have unpleasant odours. For biological treatment of tannery waste, mostly activated sludge process (ASP), and up flow anaerobic sludge blanket (UASB) process are used. ASP based treatment is considered to be energy demanding and expensive from an operation and maintenance point of view. High levels of heavy metals could affect the qualitative as well as quantitative composition of microbial communities. Several studies have found that metals influence microorganisms by harmfully affecting their morphology, growth and biochemical activities resulting in decreased biomass and diversity. Long term and short term stresses such as high pH temperature or chemical pollution often result in altered metabolism, species diversity and plasmid incidence of soil bacterial populations. Rising appeal of environmental friendly technologies has lead to the search for low cost alternate. Biological approach appears to be efficient, economical and cost effective for effluent treatment. Treatment of tannery waste water is carried out by chemical, physical, biological or combination of these methods. In the effluent organic carbon is used by aerobic microorganisms and convert it to biomass and carbon dioxide. Along with high energy utilization large amount of sludge is also generated in the process. Activated sludge treatment is most widely used with extended aeration. It is an aerobic biological process, in which microorganisms convert oxygen-demanding organic compounds into environmentally more acceptable forms.

Ganesh et al treated tannery effluent by using Sequencing batch reactor. The reactors contain two exits: one for sludge withdrawal and the other for cleaning and emptying the reactor. Sludge was introverted directly from mixed liquid at the end of the aerobic phase. Anaerobic treatment of tannery wastewaters will be noticed in the future due to the warm climate of emerging countries.

Song et al used upflow anaerobic fixed biofilm reactor (UAFBR) for treatment of tannery effluent. El-Sheikh et al treated tannery effluent with the help of Upflow anaerobic sludge blanket reactor (38).

Zupancic and Jemec used anaerobic sequencing batch reactor. Primarily, up-flow anaerobic filters (UAF), UASB reactors and down-flow anaerobic filters (DAF) used in laboratory or pilot scale for anaerobic treatment.

Song et al developed an up-flow anaerobic fixed biofilm reactor (UAFBR) to treat tannery wastewater and obtained good COD and TSS removals even under conditions of temperature shock.

Lefebvre et al used up-flow anaerobic sludge blanket reactor to study anaerobic digestion of tannery soak liquor and achieved 78% COD removal at hydraulic retention time (HRT) of 5 days, and a total dissolved solids (TDS) concentration of 71g/l. The choice of wastewater treatment process depends on several factors like cost, efficiency and environmental capability. Moreover, the wastewater characteristics should also be considered when choosing the best process. The efficiency of bioremediation is often a role of the microbial population or consortium and how it can be augmented and sustained in an environment. Microbes (bacteria/fungi) are the most significant eco-friendly agents for the degradation and detoxification of industrial pollutants. A microbial consortium is a mixture of more than two microbial species. In nature, microorganisms do not exist in isolated form sometime and somewhere they coexist with different microorganisms and established relationships that have an effect in the biological competence of all interacting species. Microbial consortia are universal in nature. They are associated in environmental remediation and wastewater treatment. Microbial consortia are more vigorous to environmental variations and are able to survive in nutrient limitation better because members of the consortium correspond with one another by exchanging metabolites or by trading molecular signals, each population or individual identifies and act in response to the presence of others in the consortium. Due to this property microbial consortium can serve obscure functions rather than individual population. This communication empowers the important feature, the division of labor among consortium population.

Subramani et al and Durai et al among all the industrial effluents, the effluent from the tannery industry possesses a major problem. Impact of tannery sludge on environment has been widely studied.

Nakatani et al applied tannery sludge to agriculture soil and studied changes in microbial activity, they also studied changes in genetic formation of bacteria in agriculture soil.

Aceves et al studied effects of tannery sludge on C and N mineralization and microbial activity in semi-arid soils.

Bosnic et al reported that low level of exposure to the gas (hydrogen sulphide) induces nausea and headaches as well as possible damage to the eye, while higher levels may cause death.

Febriana et al reported skin complaints, respiratory Disorders and low-back trouble among tannery workers in Kanpur, India. Chromium is the leading tanning agent. Most tannery and other leather product wastes have considerable amounts of chromium, which is present utterly as Cr(III) salts. Chromium hinders the growth of fish, plants and bacteria in surface waters; high levels can lead to breakdowns in cell structure. At low concentrations, trivalent chromium has a toxic effect upon daphnia, thus disturbing the food chain for fish life and possibly inhibiting photosynthesis.

Shakir et al concluded that hexavalent chromium and tannery waste have considerable potential of eco-damaging. Soaring levels of chromium are posing a considerable risk to the aquaculture, agricultural industry and human population, which can destroy ecology nearby the tanneries.

Tariq et al revealed high levels of chromium in tannery effluent and concluded that high Cr levels are hazardous for human health, especially Cr(VI).

Srivastava et al achieved 90% and 67% removal of chromium and PCP from tannery effluents by sequential bioreactor where they treated effluents by *Pseudomonas aeruginosa*, *E. coli*, and *Acinetobacter* sp.

Abskharon et al studied the reduction of hexavalent chromium to trivalent chromium by using four resistant strains of *E. coli* ASU, 3, 7, 8 isolated from waste water.

Panda and Sarkar examined bioremediation potential of *Acinetobacter* sp.PD12 and *Enterobacter* aerogens and used them to uptake chromium from tannery effluents.

Pillai et al, Smrithi and Usha isolated *Bacillus subtilis* P13 and *Bacillus* sp. respectively from tannery effluent which reduced 85.9% chromium.

Benazir et al studied ability of *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Saccharomyces cerevisiae* in accumulation, detoxification, degradation and absorption of chromium in tannery effluents and found that all strains are able to remove 99% chromium.

Chen et al isolated *Marinobacter*, *Pseudochrobactrum*, *Shewanella*, *Psychrobacter*, *Microbacterium* and *Agrococcus* strains from tannery waste which showed significant Cr (VI) removal (1.2%-99.1%) competence and good potential for Cr (VI) pollution treatment.

Poornima et al isolated chromium degrading bacteria, *Pseudomonas putida* and *Pseudomonas plecoglossicida*, from rhizosphere soil of Amrithi forest region, Tamilnadu by enrichment method.

Sau et al reported a highly chromium resistant *Bacillus firmus* strain in soil samples with chromium effluents. This strain was able to remove 80% Cr.

Farag et al isolated four chromium-resistant bacteria from tannery effluent collected from Burgelarab, Alexandria, Egypt. Two isolates were identified as *Acinetobacter* and *Pseudomonas* and they remove 66.4% Cr from effluent.

Selvi et al was evident that various bacterial strains such as *Pseudomonas*, *E.coli*, *Alcaligenes*, *Flavobacterium* and *Bacillus* species isolated from tannery effluent collected in and around Chennai, South India, showed tolerance to chromium up to 70%.

Goumghar et al recovered *D. hansenii* a yeast species from tannery wastes which was resist to chromium.

Onyancha et al demonstrated that *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*, algae biosorbants, removed chromium from tannery wastes.

Wang et al illustrated the ability of using the indigenous sulfur oxidizing *A. thiooxidans* as a potential aspirant for microbial removal of chromium from tannery sludge because of its high chromium solubilization efficacy.

Srivastava and Thakur studied biosorption and biotransformation of chromium by *Serratia* sp. isolated from tannery waste water.

Masood and Malik investigated 99% biosorption of hexavalent chromium by *Bacillus* sp. FM1, isolated from soil irrigated with tannery waste.

Fabbricino et al investigated the use of crustacean shells for the removal of chromium from tannery wastewater. *Aspergillus* sp. was used by Srivastava and Thakur for the removal of chromium at different temperature, pH, carbon, inoculum size and nitrogen source.

Sharma and Adholeya removed chromium from tannery effluent by using *Paecilomyces lilacinus* fungi.

Fadali et al removed chromium from tannery effluent by using synthetic chromium salts (chromium chloride) as adsorbate, and cement kiln dust (a waste from white cement industry) as adsorbent.

Low et al removed trivalent chromium from tannery effluent by using Moss.

Esmaeili et al reported that chromium precipitation is a relatively simple technique in which chromium and other metals are precipitated as highly insoluble hydroxides. Algae namely *Spirogyra* and *Rhizoclonium hieroglyphium* were employed to remove chromium from tannery effluent.

Poulopoulou et al removed chromium from tanned leather waste by physical (irradiation) and chemical methods.

Midha and Day removed sulphide from tannery effluent by aerobic and anaerobic treatment. They used *Thiobacillus*, *Pseudomonas*, *Beggiatoa* and *Thiothrix* for sulphide removal by oxidation processes.

Genschow et al also removed sulphide from tannery waste water by using two stage anaerobic treatment.

Goltara et al used a Membrane Sequencing Batch Reactor (MSBR) to treat sulphide compounds in tannery waste water.

Aguilar et al used an artificial wetland as the tertiary treatment of tannery waste and isolated sulfur oxidizing bacteria, which belonged to the genera *Ochrobactrum*, *Acinetobacter*, *Alcaligenes*, and *Pseudomonas*.

Vidyalakshmi et al isolated *Thiobacillus* a sulphur oxidizing bacteria from different samples such as tannery effluent, sewage, biogas slurry and mine soil.

Mullick et al isolated *Pseudomonas aeruginosa* and *Micrococcus yunnanensis* from tannery waste and carried out sulphate removal in bench top fermenter. *Pseudomonas aeruginosa* showed 240mg/L Cr and 280mg/L sulphate resistance.

Rajalo et al applied soft electrochemical oxidation method for the removal of sulphide compounds from tannery wastes.

Samanta et al studied the impact of tannic acid on the gastrointestinal microflora. According to Samantha tannic acid inhibits the activity of enzymes of rumen microbes. If large amounts of tannin-containing plant material, such as leaves of oak (*Quercus* sp.) and yellow-wood (*Terminalia oblongata*) are consumed then hydrolysable tannins are toxic and cause poisoning in animals.

Jadhav et al concluded that tannic acid is toxic to plants. Ilori et al isolated a tannic acid degrading strain of *Bacillus* sp. AB1 from a garden soil from the University of Lagos, Nigeria. This organism was able to utilize 1% tannic acid. Jadhav et al isolated *Klebsiella* sp NACASA1 from the garden soil of botanical garden of N.A.C. & S. College, Ahmednagar, India which was able to rapidly degrade tannic acid at 15°C.

Hernandez et al evaluated and isolated tannin degrading fungal strains *Penicillium commune*, *Aspergillus niger*, *Aspergillus rugulosa*, *Aspergillus terricola*, *Aspergillus ornatus* and *Aspergillus fumigates* from Mexican desert.

Nitiema et al isolated a tannic acid degrading streptococcus sp. from anaerobic shea cake digester. Knudson was first to report that tannic acid could be degraded by a strain of *Aspergillus niger*.

Chowdhury et al isolated *Pseudomonas citronellolis* from tannery soil samples, which is capable to degrade tannic acid and also studied molecular diversity of isolate.

Murugan et al isolated *Aspergillus candidus* MTCC 9628 from the biomass of mango industry solid waste. They isolated tannase enzyme from *Aspergillus candidus* which were found to degrade tannin content of the tannery effluent.

Pepi et al isolated *Serratia* spp. and *Pantoea* sp. from olive mill waste mixtures which degrade tannic acid.

Mahadevan et al studied tannin degradation with reference to aquatic microorganisms according to them tannins inhibits microbial growth, metabolism and respiration.

Bhat et al reported that species of *Bacillus*, *Klebsiella*, *Pseudomonas*, *Aspergillus*, *Penicillium* and *Trichoderma* degrade tannins.

Szpyrkowicz et al used a combination of electrochemical and biological processes for tannery wastewater treatment.

Farabegoli et al, Ganesh et al and Zupancic et al digested tannery waste by anaerobic sequencing batch reactor process and they concluded that tannery wastes are suitable substrates for biogas production.

Iaconi et al treated tannery wastewater by combining discontinuous biological degradation, in a sequencing batch biofilm reactor (SBBR), with chemical oxidation, by using ozone.

Mannucci et al and El-Sheikh et al studied biological tannery waste water treatment by applying two stage UASB (up flow anaerobic sludge blanket) reactors.

Tare et al suggested that UASB system sometimes cannot be suitable for the treatment of tannery wastes.

Banu and kaliappan made an attempt to treat the tannery waste water by using hybrid up flow anaerobic sludge blanket reactor.

Subramani and Haribalaji used microorganisms particularly *Bacillus* sp., *Pseudomonas aeruginosa* and *Aspergillus niger* to reduce pollution load of tannery effluents by activated sludge process.

Munz et al applied respirometric techniques and an activated sludge model (ASM) for the characterization of tannery wastewater. Ozone and ultraviolet (UV) radiation technologies were applied to eradicate pollutants in the tannery effluents. However, the high cost of ozone is the main disadvantage of these processes. Electrochemical oxidation was also used for final tannery wastewater treatment showing complete mineralization of vegetable tannery wastewater.

Filibeli et al solidified tannery waste to reduce their environmental impacts. They mixed sludge with cement and additives and left to solidify for 28 days.

Hasegawa et al reported tannery wastewater treatment at laboratory scale using *Botryosphaeria rhodina* MAMB-05, a ligninolytic and a constitutive producer of laccases.

X. Conclusion

Based on literature the following points should be cleared,

Chemical coagulation needed additional chemicals that caused secondary pollution. There were also disadvantages for the photo-degradation of tannery waste water because of the lower energy utilization efficiency.

Although bio-degradation process was cheaper than other methods, it was less effective because of the toxicity of the tannery waste water that will affect the development of the bacteria.

Sulfate and Cr are chemically removed, but microbial treatment processes need secondary primary or secondary treatments in analysis. If the process is too long, it becomes infeasible for treating huge amount of waste generated. Often nutrient supplements need to be added for biological processes.

Compared with other methods, there were a few advantages for the treatment of tannery waste water by electro coagulation. Energy consumption could be decreased for the better conductivity due to the masses of salt and the reaction conditions could be easily controlled by changing the electro cell current or voltage.

Electrochemical waste destruction shows several benefits in terms of costs and safety. The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes.

EC technology needs better reactor design, understanding and process control in future, because of its numerous advantages and changing strategic global water needs.

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