Available Techniques of Wastewater Management Practices in Indian Tanneries: A Literature Review

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Abstract
Tanning is the process of turning animal hide into leather. The manufacturing process leads to the generation of wastewater, which must be treated before discharge. The treatment processes of this wastewater in India was examined. A systematic review based on Preferred Reporting Items for Systematic Reviews and Meta-analysis (PRISMA) guidelines was carried out on the electronic database Google Scholar from 2010 to 2020. Wastewater treatment practices in Indian tanneries were looked for and 64 relevant reports and articles were shortlisted and studied. The results showed that coagulation with alum and ferric chloride gave the best results in primary treatment, aerobic and anaerobic processes gave the best results when combined, and tertiary treated water could be reused.

Keywords: Wastewater treatment, Indian tanneries, Primary treatment, Biological treatment, Tertiary treatment, Biosorption, Membrane processes, Activated sludge process

1 Introduction
A tannery is a place where animal hides are processed or tanned with the use of various, usually harmful, chemicals to make leather (1). They are one of the most water and labour intensive and highly polluting industries today (2). Tanning involves three broad processes- pre-tanning in which hides or skins are cleaned; tanning process, which permanently stabilizes the hides and post-tanning or finishing operations, where final shape value is added for manufacturing of leather (3). The wastewater generated from these processes must be treated before discharge. The treatment of tannery wastewater leads to the generation of sludge laden with chromium that makes it hazardous (4). This sludge can lead to soil pollution if it is not disposed of properly (5).

Tannery wastewater is dark brown and it is foul-smelling, probably due to the presence of large amounts of organic and inorganic substances (6). The presence of organic compounds is characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) which deplete dissolved oxygen in the water bodies that they are discharged into (7). Besides these, high salinity, nitrogen, suspended solids, sulphate, sulphide and suspended solids make it difficult for aquatic life to survive (8,9). These chemicals make the wastewater highly acidic and are further accompanied by phosphates, calcium and magnesium (10). Chromium is one of the biggest threats to living beings especially when it is in the form of hexavalent chromium (11,12). It gets absorbed into cells faster and could accumulate in lungs kidney, red blood cell etc. and change their functionality (12).

Studies have shown that chromium and its compounds, beyond a certain level, can damage DNA by breaking its single and double-strands (13). It can also cause skin allergies, dizziness, reproductive problems among other issues as well (14). Among fishes, structural alteration could occur due to chromium (15). Not only do all of these pollutants affect aquatic life, but also the humans or animals which are dependent upon these water bodies. Groundwater pollution and soil pollution is a problem many residents living close to tanneries have to deal with (16). This makes groundwater unsuitable for irrigation and soil unsuitable for crop growth (17). Different techniques have been employed in India to treat tannery wastewater before its discharge like physical, physico-chemical, electrochemical and biological treatments. These are practised in India besides more advanced techniques like reverse osmosis (RO), ozonation and membrane processes (18).

The objective of this paper is to review the wastewater treatment techniques used in the tannery industry. The pieces of literature have been studied in details and improvement to an existing process has been suggested. A recommendation has also been provided based on the most economic option for reuse of treated water from a tertiary treatment process.

2 Background
Tanning has been carried out since time immemorial. Before the discovery of chrome tanning method, different tanning processes like aluminium tawing, smoke tanning and oil tanning were employed globally. 3000-year-old leather manufactured by
Egyptians gave evidence for oil tanning (14). However, the most popularly used method to tan hides in tanneries worldwide today is chrome tanning (2). Chrome tanning is faster and cheaper, but as a big portion of it ends up in the effluent as sludge, its disposal becomes a problem. The use of nanoparticles in tanning is slowly making its way into tanneries and silver nanoparticles have been found to render anti-microbial, UV-resistant and anti-fungal properties to leather (14).

Pollution control related measures have been adopted by Indian tanneries since the latter half of the 1980s after international bans and domestic regulations forced Indian tanneries to embrace more environmentally friendly methods of manufacturing leather. In 1996, the Supreme Court made it mandatory for tanneries to attach themselves to a Common Effluent Treatment Plant (CETP) or an Individual Effluent Treatment Plant (IETP). Most Indian tanneries now have pollution control devices (19). ETPs fall under two categories-registered and unregistered. Registered firms are required to have an on-site Primary Effluent Treat Plant (PETP) and connected to a CETP if an IETP is absent, while no such mandate has been declared for unregistered firms (1). There are close to 200 IETPs in India (20). The number of CETPs in India in 2018 was 19 with 17 of them operating in the States of Uttar Pradesh, Tamil Nadu and West Bengal. 13 of them are in Tamil Nadu, 3 in Uttar Pradesh and 1 in West Bengal (1).

To review the treatment processes, the different processes involved in tanning have to be understood first. Pre-tanning, as mentioned earlier, refers to the cleaning of hides. First, the skins are salted for prevention from rotting and this is called curing. After this, soaking is done to wash away the salt and impurities and to increase moisture. Liming and unhairing for the removal of skin proteins are done to ready it for tanning. After this, fleshing is done. This is followed by deliming and bating to remove lime and increase pH in a drum. For bating, the proteolytic enzyme is used in the same drum operation. This drum also houses the next processes of pickling and chrome tanning. Basic chromium sulphate is used for chrome tanning and this makes it one of the most polluting processes in tanning (21). If vegetable tanning is used, it occurs in two steps, penetration and fixing. The former process diffuses tannins, which comprise a complex mix of phenols, into the skin while latter binds collagen with the penetrated tannins (14). Vegetable tanning is a slower and more costly process (22). After this, in post tanning operations, neutralization and bleaching are done, followed by retanning, dyeing, and fatliquoring in a single vessel. Other properties to enhance leather properties like water repellence and abrasion proofing may be added. At last, finishing operations take place to make the hide softer and to cover natural scars or marks by treating it with an organic solvent or water-based dye and varnish (23). For every ton of hide processed, about 300kg chemicals are used (24). The wastewater released annually amounts up to 9420 kilolitres (25).

The methods to treat the wastewater generated from these processes will be covered in the results section.

3 Methodology

3.1 Search strategy

Keywords like “wastewater treatment in Indian tanneries”, “activated sludge process” and “biosorption” were used to search the Google Scholar database. A time period of 10 years from 2010 to 2020 was allotted and citations and patents were included. The search strings provided about 13,900 results, out of which 63 finally were selected and analysed. All 63 items were of an open-access type and include journal articles, book sections, conference proceedings and thesis documents. The report by CPCB on global best practices was retrieved from the India Environment Portal website.

3.2 Study selection

For screening purposes on Google scholar, the titles and abstracts were analysed and 78 articles were shortlisted. After this initial screening, the 78 shortlisted documents were screened further by checking for the location of tanneries, tannery processes, the impact of tannery effluents and methods of wastewater treatment solely in India by reading the introductions and conclusions. This resulted in the elimination of 15 papers that did not match the secondary screening parameters mentioned above. The search strings were not modified to find specific articles on tannery processes or their impacts. Thus 63 documents, comprising journal articles, book sections, conference proceedings and thesis documents, have been analysed to understand the wastewater treatment effectiveness of different processes typically used in India.

The detailed methodology with the use of PRISMA guidelines is given below:

3.3 Data collection

Data for the systematic review of wastewater treatment in Indian tanneries were collected through the 63 relevant literature articles which were examined. For a better understanding of wastewater treatment of tannery effluent, articles which were chosen covered tanning process in use today and its evolution, the impact of tannery effluent on the environment and living beings and last but not the least, wastewater treatments in use in India for the last decade. CPCB’s report was used to understand the best available techniques in tannery effluent treatment at a CETP in Tamil Nadu, India. The pros and cons of the processes from retrieved literature have been assessed to provide recommendations. Risk of bias in individual studies involves not
taking exact costs of implementation or operation of various techniques into consideration, the review of open-access documents alone and the assumption that the research techniques of multiple methods are accurate and consistent.

4 Results
4.1 Primary Treatment
Coagulation and flocculation as mentioned above, are primary treatment methods. Chemical coagulation requires the addition of coagulants which help colloidal particles to aggregate into larger-sized particles, which may then be sedimented or flocculated (26). Flocculants enable the agglomeration. This may be carried out by the use of alum or ferric chloride or the combination of both (27). Best results are achieved by the combination of both (26). For vegetable tanneries, use of poly aluminium chloride with flocculants gives good results for the removal of TSS, COD and colour (27). The use of these chemicals to treat tannery wastewater leads to the generation of toxic sludge (4). The process of precipitating contaminants by the use of the direct current in an electrolytic environment followed by flocculation with or without the addition of coagulant is called electrolycoagulation (Ahmed Samir Naje, 2013).

Table 1: Primary Treatments

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Coagulation</td>
<td>High COD, colour and turbidity reduction, Better colour and COD reduction than chemical coagulation, more robust against pH change, cheaper, more efficient, better for vegetable tanning effluent removal</td>
<td>Needs better reaction, safer, more efficient, better for vegetable tanning effluent removal</td>
<td>Saritha et al. (26), Borchate et al. (27)</td>
</tr>
<tr>
<td>Electrocoagulation</td>
<td>Oxidizes organic matter, reduces chromium (III) and dichromate ions by recycling ferrous ions</td>
<td>Generates sludge, excessive dosage and improper pH stop recycling (28) ferrous ions and lead to precipitation</td>
<td>Meenachi et al. (3), Naje et al. (29)</td>
</tr>
<tr>
<td>Electrochemical peroxidation</td>
<td></td>
<td></td>
<td>Selvabharathi et al. (30), stop recycling (28)</td>
</tr>
<tr>
<td>Biosorption: Microbial</td>
<td>Naturally available, abundant</td>
<td>Maintenance of stringent reaction conditions</td>
<td>Sivakumar (31)</td>
</tr>
<tr>
<td>Agricultural wastes</td>
<td>Cheap, abundant</td>
<td></td>
<td>Sivakumar (32,33)</td>
</tr>
</tbody>
</table>

It is also beneficial in terms of cost and safety while having high efficiency, but it needs better reactor design and there is scope for a better understanding of the process and its control (3). The use of hydroxyl ions from Fenton’s Reagent (Fe²⁺ + H₂O₂) comes under advanced oxidation processes (AOPs) and this can be carried out as a primary or tertiary treatment (28). It is prudent to remove as much chromium from the wastewater as possible because it is inhibitory to the growth of the microbes used in biological treatment (21). The removal of chromium by metabolic or physico-chemical uptake by biological materials is called biosorption (34,35). When technologies with living organisms are used to reduce the toxicity of contaminants, it is called bioremediation (7).
Many different microbes like different species of bacteria and fungi can be used bio sorbents and have been highlighted as such in many literary documents (36). Activated carbon was used earlier but it is expensive and other alternatives have been explored (37). Constructed wetlands are wetlands with controlled environments used for filtering, volatilizing, microbial-mediated processing (MMP), sedimentation, sorption, and many more. Biochar from heated coconut shell can be used as an adsorbent in constructed wetlands (49). Though constructed wetlands are low cost, they are discouraged in India due to odour issues (20).

4.2 Secondary Treatment

Secondary treatment involves activated sludge-based treatment, forced aeration by surface aerators and recycling of activated sludge (Manikant Tripathi S. K., 2019). It is carried out via biological means to treat organic effluents in the wastewater and can be done by aerobic, anaerobic or anoxic processes (18). Aerobic processes do not release odour but they release a huge amount of sludge. The salinity of tannery wastewater can also hamper the treatment process. Anaerobic treatments are more favourable in tropical environments and they generate less sludge and consume less energy (22). Their efficiency can be monitored by their ability to generate biogas (50). Activated sludge processes (ASPs), Sequential batch reactor (SBR), Up flow anaerobic sludge blanket (UASB), Membrane Sequential Batch Reactor (MSBR), Up flow Anaerobic Fixed Biofilm Reactor (UAFBR) and Sequential Batch Biofilm Reactor (SBBR) are used in biological treatment (20).

Activated sludge comprises microorganisms in an aerated environment and for designing an ASP reactor, factors like influent flow rate, surface area, length and scour velocity are taken into consideration (25,51). At Unnao, in Uttar Pradesh, India, a CETP is present that employs ASPs. In it, large particles are first screened and then mixed completely by air diffusers at the bottom of an equalization tank. The effluent is then pumped into the flash tank for pH adjustment through chemical dosing. After this, suspended solids settle by floc formation and it is removed. Effluent is then treated aerobically in aeration tanks and colloidal particles, that settle down in clarifiers is drained through terminal main hole (52). The use of pure oxygen with a catalyst (manganese sulphate) aids sulphide reduction and it has been observed with oxygen injection with manganese sulphate as a catalyst in aerated conditions, not in a UASB reactor (53). The same could be combined to increase the UASB’s efficiency.

UAFBR can also be used as an alternative to other anaerobic technologies although sulphur toxicity needs to be taken into account before its administration (20).

Biofilm reactors have good specific removal rates due to the higher concentration of biomass. An SBR combined with ozonation can remove COD, NH$_4$-N and TSS up to 97%, 98% and 99.9%, respectively (20,53). Sulphate reduction can be achieved through sulphate-reducing bacteria. MSBR has proven to reduce ammonium and COD after sulphur from the tannery wastewater has been removed by oxidation. The cost of this technology may, however, make it difficult to implement (20).

Table 3: Comparison of biological treatment performances

<table>
<thead>
<tr>
<th>Method</th>
<th>Untreated Effluent</th>
<th>Treated Effluent</th>
<th>Reduction</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 8.1±0.1</td>
<td>pH: 6.8±0.1</td>
<td>88.9</td>
<td>Ramteke et al. (52)</td>
<td></td>
</tr>
<tr>
<td>COD: 2016±2.0</td>
<td>COD: 224±1.0</td>
<td>97.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOD: 1520±10.0</td>
<td>BOD: 40±5.0</td>
<td>86.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr: 62.38 ± 88.21</td>
<td>Cr: 5.48 ± 2.42</td>
<td>95.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td>COD: 1908</td>
<td>Mg/L 343.44-381.6</td>
<td>80-82%</td>
<td>Suresh et al. (55)</td>
</tr>
<tr>
<td>SBBR+COD</td>
<td>OzonatiNH$_4$-N on TSS</td>
<td>NK</td>
<td>98</td>
<td>PC (20)</td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>90</td>
<td>99.9</td>
<td></td>
</tr>
<tr>
<td>MSBR</td>
<td>Ammonium Nitrogen</td>
<td>Mg/L 550</td>
<td>100-100</td>
<td>PC (20)</td>
</tr>
</tbody>
</table>

NK-Not known

4.3 Tertiary Treatment

For tertiary treatment, RO, ultrafiltration (UF), ozonation and phytoremediation may be carried out. Membrane processes include microfiltration (MF), nano-filtration (NF), UF and RO (22). Chemicals may also be used to get rid of COD (57). They can help in the recovery of chromium which can be used again for tanning (22).

One of the first polymeric membranes to be used for UF or RO was cellulose acetate, along with a pore-forming agent, synthetic polyether polyethylene glycol (PEG). Clogging of the pores due to the effluents being subjected to the membrane for an extended period can reduce its efficiency to remove chromium. At an appropriate pH, chromium reduction with a novel UF membrane made from cellulose acetate, polyethylene glycol and nanochitosan can vary from 90% to 39% depending on the contact
time and subsequently varying porosity of the membrane. Similarly, BOD and COD reduction of 56% and 51% respectively have been observed after an extended contact time. The maximum removal of chromium was noted at neutral pH with a membrane thickness of 0.2mm and 100kPa pressure and industrial application of this has been suggested (58).

Low pressure, polymeric membranes may be used for MF or UF for providing RO feed water but tannery wastewater contains fine suspended solids which can block pores of these membranes and lead to permanent fouling because it is difficult to clean. Turbidity should be maintained below 1 nephotometric turbidity units (NTU) to prevent the permanent fouling of these membranes. Ceramic MF membranes are more advantageous than polymeric membranes as their high porosity supports the separation of higher turbidity and colloidal impurities to produce good feed for the RO process. Ceramic membranes can even be used for pre-treatment of raw tannery wastewater as this will reduce the steps involved in conventional treatment. Following this with RO through the polymeric membrane can produce permeate suitable for reuse in the tanning process. Leather produced with the aid of treated water has been reported to have better physical properties in terms of dye acceptance and tensile strength as compared to leather manufactured by freshwater. A reduction of 91% in COD and BODs, 62% in total organic carbon (TOC) and turbidity reduction below 1 NTU was observed after MF. After RO, 99% of TOC, 82% of sodium and turbidity reduction to 0.025 NTU was achieved (59). Phytoremediation uses plants in constructed wetlands to convert toxic compounds into non-toxic compounds. It has aesthetic advantages and it is sustainable but it can only be used for water with low contamination (22). RO treatment is expensive but it can give fantastic results for the removal of TDS and chlorides (60). One of the main disadvantages of membrane processes includes the biofouling of the membrane.

Ozonation and the use of ultraviolet (UV) radiation fall under advanced oxidation processes. Hydrogen peroxide can also be used for this, along with catalysts like iron, manganese and titanium dioxide (TiO₂). These treatments are expensive, but stringent regulations are making them popular and their cost is also decreasing (22). Even though solar energy can be used to harness UV as a cost-effective method, photocatalysis by combining TiO₂ and UV rays achieve high efficiency only under high UV irradiation. Adding the Fenton reagent to this improves the efficiencies of both the systems by increasing lifetime and generating more reactive radicals. Combination of biological treatments and AOPs have been suggested as pre-treatment or post-treatment for increasing the efficiency of the treatments as well as reducing the costs (28). Integration of membrane processes with photoelectrooxidation has been suggested to enhance the reduction of COD levels in tannery effluent (53).

The CETPs in Tamil Nadu, with their zero liquid discharge (ZLD) policies, have fared better as compared to CETPs in Uttar Pradesh and West Bengal not only for wastewater treatment but also in terms of waste management post-production (1).

The achievement of ZLD requires water recovery and thermal evaporation of saline reject from RO (61). The saline reject from RO may be disposed into the sea but under control, while recovered water will help to deal with its shortage (62). There are tanneries in Tamil Nadu, that employ the RO process for wastewater treatment and the performance of some of them have been studied. The permeate capacity of each of the plants are different, but all of their rejects are sent for solar evaporation first and some reuse the permeate in their tanning processes (60). An expensive alternative to solar evaporation is multiple effect evaporators (MEE) (61). The wastewater streams in these tanneries are separated into chrome containing wastewater, high BOD and COD wastewater and high inorganic salt encompassing wastewater. Conventional treatment after chromium recovery reduced BOD by 93-95%, sulphide by 70-86.4% and complete removal of chromium. TDS removal was however negligible by conventional methods. TSS, BOD and COD from RO permeate has been reported to be below detection level (BDL) in some tanneries. MBRs combined with RO can reduce TDS by 91.1% (60,62). To achieve TDS discharge norms of composite tannery effluent, tertiary treated effluent from tanneries is mixed with treated effluent from slaughterhouses and domestic wastewater from nearby areas (61). This mixture is also being used for green development in some landlocked areas (63). Tanneries in Vaniambadi, Tamil Nadu practice preliminary treatment before their wastewater is sent to the CETP for further treatment. This CETP treats effluents from 130 tanneries. Chrome and non-chrome water are treated separately in the individual tanneries for better treatment of water. Chrome water is treated in chrome recovery units at individual tanneries. The primary treatment includes mechanical screening and alum dosing with polyelectrolytes. Clarifier liquid from this is sent to a storage tank and conveyed to an anoxic tank after fine filtration. From there it is moved to an aeration tank and then to MBR. The effluent is then given RO treatment. As mentioned earlier in this review, RO does away with TDS which falls below 500mg/L. The permeate can be reused and the reject can be evaporated to recover salts. Implementation of MBR combined with RO in other CETPs or IETPs in India can result in 100% elimination of suspended solids as compared to the global average of 96.5% and large mitigation of chlorides by 97.8% as compared to the global average of only 36.5% (2).

5 Discussion
This literature review provided a comprehensive understanding of major wastewater treatment methods used in Indian ETPs. The treatment processes include physico-chemical processes, biological processes and membrane processes that broadly come under primary, secondary and tertiary treatments. Combination of chemicals in coagulation provides best results in primary treatment but it may prove to be costly due to increased chemical use. The combination of aerobic and anaerobic treatments provided the best results in biological treatment. Preliminary separation of chrome and non-chrome water along with the combination of MBRS with RO techniques after primary chemical treatment has produced the best results in terms of pollutant reduction as acknowledged by some authors in reviewed literature as well as by CPCB. Membrane processes are expensive, but the quality of treated water obtained can be reused to reduce the freshwater footprint of a tannery and evidence has been given that the treated water imparts better physical characteristics to leather than freshwater. The adoption of this technique by more CETPs and IETPs will help the Indian leather industry to become eco-friendlier and more sustainable.

6 Way Forward
There are several technologies available in India to treat the
wastewater generated from tannery industries. Screening and grit removal can be practised before primary chemical coagulation and flocculation. The combination of alum and ferric chloride has given the best results.

In secondary treatment, the selection of technology depends on basic criteria like the desired and initial effluent quality, the area available, and the budget and cost for construction and operation of the treatment plant. For anaerobic reactors, especially UASB, sulphur content may be reduced by oxidation through injection of manganese sulphate as a catalyst if deemed economically feasible.

Tertiary or advanced treatments can only be recommended for the reuse of treated water. The treated effluent can be reused after removal of ions by passing through the RO membrane. RO reject handling and its treatment, and proper disposal is very tedious and costly because of higher TDS content. The RO reject may be used for irrigation after it is blended with the treated sewage water. TDS discharge norms in Tamil Nadu are already met by mixing treated tannery wastewater with domestic wastewater as mentioned earlier in the review. The dilution or treatment of sewage and tannery effluent must not be done together in anaerobic conditions (64). Aerobic processes are recommended for this. This treated effluent can be reused very economically after the blending ratio is decided, based on the TDS of treated effluent and treated sewage.

7 Conclusions

The main findings of this literature can be summarised as follows:

- Tannery effluent may be treated physico-chemically, chemically or biologically.
- The results of chemical coagulation are better when alum and ferric chloride are mixed instead of being used individually.
- Combination of the aerobic and the anaerobic processes gives the best results in the biological treatment step.
- Wastewater treated with the help of RO can be reused in the tanning process to reduce the freshwater footprint.
- The TDS in the RO reject can be diluted by mixing with treated domestic wastewater and used in irrigation or discharged.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, conflicting interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The author declares that there is no conflict of interest that would prejudice the impartiality of this scientific work.

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