CHAPTER I

INTRODUCTION

1.1. Leather industry

Indian leather sector is the significant foreign exchange earner besides it provides large employment potential to economically weaker section. Moreover, leather sector contributes intangible benefits to environment by converting the putrescible raw hides/skins into non-putrescible leather.

The unique aspect of Indian Leather sector is that it turns out best possible quality leathers from relatively poor quality hides/skins. The annual production of finished leather in India is about 180 million sq. m which accounts to be 12% of global production. The state wise distribution of tanneries in India (total number of tanneries are 3000) are Tamil Nadu, 50%; West Bengal, 20%; Uttar Pradesh, 15% and Punjab, 8% [1].

The presence of moisture makes the hides/skins very liable to microbial attack. Putrefying bacteria degrade the hides/skins causing damage to both grain and flesh side of the pelt and leads to greater degree of degradation. Generally salt (30 – 40% on raw hide/skin weight basis) is applied on flesh side of hides/skins to overcome microbial attack. One ton of raw hide/skin produces 250 kg of finished leather besides generation of wastewater (48 m³), and solid waste containing sodium chloride (200 kg), and
organic salts (2-4 kg) [2]. The slaughter houses that supply raw skins/hides are located far from tannery clusters in India, thus indicating the necessary protective mechanism during transportation and storage of them. The problem is being addressed in India, by preserving the hides/skins with common salt at abattoirs or at local collection centers. India imports hides/skins from other countries in the wet salted conditions in order to manage the raw material shortage. Traditional leather processing employs chemicals over their stoichiometric requirement higher by 40-75% [3]. Hence, the wastewater generated from leather industry contains huge amount of sodium chloride besides other inorganic and organic salts.

The organic salts present in the tannery waste waters are treated by following conventional treatment steps: primary clarification, secondary biological anaerobic/aerobic treatment, and tertiary treatment processes [4, 5].

1.2. Importance of membrane separation process in tannery waste water treatment

The tannery wastewater after secondary biological treatment contains high amount of inorganic salts collectively known as (TDS), besides dissolved organics expressed as BOD$_5$ and COD (Table 1.1). Membrane separation processes have become a competitive option for the tertiary treatment of secondary biological treated tannery wastewater for the removal of TDS. Membrane separation processes are easy to operate; they go by modular construction and smaller footprint requirement besides outstanding quality of product water for reuse. Hence, Reverse Osmosis (RO) process has been made mandatory in southern part of India for recovery of water from
secondary biological treated tannery wastewater and leaving behind refractory organic and inorganic salts in the reject stream. The reject stream is evaporated in multiple effect evaporator (for Common Effluent Treatment Plant) or solar evaporation pan (for effluent treatment plant).

**Table 1.1 Characteristics of Untreated, treated, RO permeate and RO reject stream in leather industry**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Untreated waste water</th>
<th>Biological treated wastewater /RO feed</th>
<th>RO Permeate</th>
<th>RO Reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Dissolved Solids</td>
<td>7.67 ± 4.08</td>
<td>5.58 ± 1.80</td>
<td>0.25 ± 0.13</td>
<td>20.0 ± 6.14</td>
</tr>
<tr>
<td>Biological Oxygen Demands</td>
<td>2.09 ± 1185</td>
<td>0.10 ± 0.091</td>
<td>-</td>
<td>0.40 ± 0.32</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>4.76 ± 2.42</td>
<td>0.43 ± 0.29</td>
<td>0.005 ± 0.007</td>
<td>1.53 ± 0.85</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.60 ± 1.44</td>
<td>1.65 ± 0.53</td>
<td>0.05 ± 0.02</td>
<td>3.96 ± 1.67</td>
</tr>
<tr>
<td>Chloride</td>
<td>1.30 ± 0.42</td>
<td>1.30 ± 0.40</td>
<td>0.07 ± 0.02</td>
<td>4.99 ± 2.20</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2.67 ± 1.58</td>
<td>2.31 ± 1.25</td>
<td>0.01 ± 0.02</td>
<td>5.55 ± 1.95</td>
</tr>
</tbody>
</table>

* All the values are expressed in g/L, except pH.

**1.3. Characteristics of membrane concentrate**

Membrane separation is a physical process involving the separation of particulate, and dissolved organic/inorganic compounds from a feed liquid using a semi-permeable membrane system. As a result of this treatment, the feed stream is fractioned into two streams (i) a permeate stream that contains the solvent that passes through the membrane, and (ii) the reject stream known as concentrate, reject or brine contains the
solute. The characteristics of this reject stream depend primarily on the membrane technology used, the quality of feed water, the percent recovery of water, the physico-chemical treatment methods followed and cleaning procedures. The volume of reject stream varies widely from 10% to 60% of the feed water volume [6]. The reject stream arises from tannery effluent is turbid and opaque, may be due to the presence of micro and macro organic molecules and inorganic ions, such as chlorides, sulphates, phosphate, carbonate, bicarbonate, sodium, calcium, magnesium and other heavy metal ions [7].

1.4. Impact of membrane concentrate discharge without treatment

Discharge of RO reject stream into seawater is considered to cause the "sea desert" in vicinity to pipe outlet because dissolved substance with high specific weight sink in bottom of the ocean, severely affecting local marine biota. Marine species have been affected by the salinity of the brine discharged into the sea include grass prairies called Cymodoceanodosa and Caulerpaprolifera or red algae [8]. The number of tanneries in India is approximately equal to 3000, among which 50 % of the tanneries are located in Tamil Nadu. The generation of wastewater from the CETPs located in Tamil Nadu was accounted to be 17.65 MLD. Amongst the 13 available CETPs only 10 CETPs have zero liquid discharge option with RO rejection volume of 3MLD (appx.).

Direct land disposal of RO reject stream from effluent treatment plants caused soil and groundwater contamination by the diffusion of organic impurities from it, and thus soil and ground water are turned unsuitable for human consumption for their
harmful or toxic substances. Hence, there has been exploration to manage the RO reject stream.

1.5. Options for membrane concentrate disposal

Various options have been reported for the disposal of RO reject stream generated in membrane separation of tannery wastewater. They may include discharge to surface water, deep wells, evaporation ponds, and wastewater evaporators. The selection of technologies for the disposal of RO rejects is based on the prevailing environmental regulations, investment and maintenance costs, and site-specific conditions [9, 10].

Crystallizers and spray dryers have been implemented at the commercial level to reduce RO reject stream into a solid product for landfill disposal. One or more evaporation steps could also be considered to recover small amounts of water from the most soluble salts in RO reject stream [11].

The evaporators and crystallizers are used to reduce the reject volume upto 5% of the feed volume and the rest 95% was reclaimed as distillate (water) after condensation.

Generally, the reject stream generated from leather industry is evaporated in solar evaporation pans to reduce its volume (for small volume of discharge and making use of solar energy to reduce the cost of evaporation) or in a multiple effect evaporator (MEE) (for large volume of discharge) leaving behind a solid residue known as residue
after evaporation (RAE). The theoretically calculated RAE mass was found to be 250 tonnes per day from reject stream of membrane separation process implemented in Leather industry, Tamil Nadu.

1.6. Limitations on disposal of residue after evaporation generated from leather industry

The disposal of RAE onto secured landfill sites is banned by the pollution control agencies because the constituent ions are suspected to be leached into aqueous solution, and the treatability of leachate would be more difficult for its high salinity. Hence, RAE is collected and being stored in the storage yard without reuse options and leather industry confront with land availability to manage the progressive generation of RAE. The high concentration of inorganic and organic salts present in RAE restrains it from disposal [12, 13]. Thus, there has been a constant research for the management of RAE.

1.7. Recovery of inorganic salts from RAE

The recovery of salts and other minerals from RAE is the most obvious solution to eliminate the disposal problem. However, no single report is available on the recovery of chloride as sodium chloride and sulphate as calcium sulphate from RAE generated in leather industry. The presence of organic salts in RAE retards the process of recovering the inorganic salts from it. Thus, an attempt was made in the present investigation to precipitate chlorides and sulphates as sodium chloride and calcium sulphate selectively in the presence of organic compounds [13, 14].