CHAPTER 1

INTRODUCTION

1.1 INDUSTRIALIZATION

Rapid industrialization and improved life style have consequently led to increase in the quantity of wastewater discharged into the environment (Dutta 1999; Miller 2001; Sawyer 1994). The wastewater released from chemical process industries has potential hazard to the environment due to its contaminants such as high COD, heavy metals, oil and grease, VOC, color etc., (Sarkar 1997; Adams 1990; WHO 2004), which is major concern among industries/researchers and environmentalists. Today, humans are inducing environmental changes in the planet as a whole. The waste minimization/water conservation in recent years has also resulted in addition of toxic residues in the environment. The paramount importance of environmental challenges is to dispose off these residues through proper technique and keep the pollutant level in the effluent stream below the tolerant limit to comply with environmental norms. The release of pollutant differs from industry to industry (Parag et al 2004; Praveen et al 2010; Chithra et al 2008; Ali 2001). Though India has implemented relatively stringent environmental regulations, the country continues to encounter enormous environmental problems, many of these due the result of industrial activities. This is also the case with leather tanning industry.
1.2 TANNERY INDUSTRY

The Indian leather industry is a large player in the global market, and a major source of foreign exchange revenues. India is the third largest leather producer in the world, behind China and Italy. Tanning industry contributes significantly towards exports, employment generation and occupies an important role in Indian economy. On the other hand, tannery wastes are ranked as the highest pollutants among all the industrial wastes. The process of tanning requires large amount of fresh water and various chemicals. More than 300 litres of water is required for every 10 kg of raw skins processed. Similarly, for every ton of skin processing, about 300 kg of chemicals are required (Verheijen 1996). The tanning process consists of a sequence of mechanical and chemical processes in which the animal skins and hides are converted into leather products (Mondal et al 2005; Chandramouli, 1998; Gopalakrishnan, 1999; Dhayalan, at al. 2006; Wiegant et al 1999; Oke et al 2006; Sreeram and Ramasami 2003; Stoop 2003; Sharphouse 1983). There are four basic stages in the tanning process: preliminary processing, tanning, post-tanning and finishing.

1.2.1 Preliminary Processing

In preliminary processing, the raw material is prepared for tanning through various cleaning/conditioning steps:

- Soaking: removes dirt and impurities, blood and preservatives (NaCl), helps the hide to regain their normal water content, softness and shape
- De-hairing: removes hair, wool and keratin from the hides.
- Deliming: removes excessive lime used in de-hairing by \((\text{NH}_4)_2\text{SO}_4 / \text{CO}_2\).
• Bating: eliminates the impurities by adding enzymes.

• Pickling: reduces hide pH, which favors tanning. The low pH condition also inhibits the enzyme activities. In pickling, salts are added to prevent the hides from swelling.

The wastewater generated from preliminary processing contains excessive chemicals, animal residues such as hair and fleshing sludge.

1.2.2 Tanning

Tanning is the process which converts animal hides into leather. In this process, the leather is made resistant to biological decay by stabilizing the collagen structure of the hide, using natural or synthetic chemicals (UNEP 2004). The hides and skins have ability to absorb other chemical substances, which make the hide resistant to wetting and prevent decaying. During the tanning phase, the tanning agents interact with the collagen matrix of the hide, stabilizing both the collagen and proteins. The leather thus attains resistance towards chemical, thermal and microbiological degradation. The tanning can be done either with vegetable tanning agents such as bark from the quebracho (Argentine) or chemically with chrome. After tanning, the hides are split horizontally into an upper layer called the grain, and a layer from the flesh side called the split. These layers are separately processed further, sometimes retanned and then pressed, stretched and dried. The waste stream generated from tanning process contain excess tanning agent, and trace of hide residue (Dhayalan et al 2006; Rameshraja and Suresh 2011).

1.2.2.1 Chrome Tanning

Leathers are generally produced by chrome tanning. It consumes less processing time than traditional vegetable tanning. The chrome tanned leather is better suited for various applications, particularly for the upper parts
of boots and shoes. No two tanneries are identical; each has its unique characteristics and subprocesses. Some tanneries perform only certain processes and ship their goods to another tannery to complete the processing. As stated earlier (preprocessing), the hides are received from meatpacking plants by truck or railroad car. The hide bundles are cut open and the hides are unfolded, inspected, and usually split along the backbone, producing two sides from each hide. The hides are soaked in water to return some of the lost natural moisture. The hides are then soaked in a lime and sulfide solution which either loosens or dissolves the attached hair. In some operations, the hair is only loosened through the caustic action of the lime, with the hair removed mechanically, followed by washing, drying, and sold as a by-product (for carpet pads and similar uses). The hides are now ready for actual tanning operation. The hides are placed in large rotating drums and treated in turn with an enzyme solution and then a salt-acid solution (bating and pickling) to prepare the hide for the tanning process. Chromium sulfate solution is added to the drum and the hides and chrome solution are mixed for about 24 hours. The excess moisture in the hide after tanning is removed through wringing operation. The cattle hides are too thick for most purposes so the tanned hides are split using a machine similar to a horizontal band saw. The splitting operation yields a thin, inner portion of the hide known as a "split" or "blue drop." Splits have no graining and are often used for garments. Both the grain side and the split may be further processed to form a piece of material of uniform thickness. This operation is called shaving and results in the removal of small pieces of leather with a consistency similar to very coarse sawdust. The tanned hides are further placed into another drum to produce a further stabilization of the collagen network called retanning. Retanning is shorter tanning operation normally done with tanning agent other than chromium. The fiber elements dehydrated by tanning are coated with a fat layer to give leather the desirable softness called fat liquorizing. The fat liquorizing influences
the physical properties of the leather, such as extensibility, tensile strength, wetting properties, waterproof and permeability to air and water vapour.

1.2.2.2 Vegetable Tanning

Vegetable tanning uses the extracts from various tree barks as the tanning agent. Since the introduction of chrome tanning, the vegetable tanning has lost its importance in tannery operation. Many of the basic steps used in the chrome tanning process present in vegetable tanning except some changes in the sequence of processing. The hides are soaked in lime to loosen the hair and subjected for fleshing operation. After fleshing, the hides are trimmed into a roughly rectangular shape and then passed through pickle operation similar to that is used in the chrome tanning process. The hides are then colored with tanning solution. In general, the vegetable tanned leather is not strongly colored. The colored hides are placed into vats containing the bark extract tanning solution and moved from a strong tanning solution to a slightly weaker one, then rinsed and partially dried. In vegetable tanning, a process called leveling is practiced in the place of true splitting to produce uniformly thick leather. Then the hide is oiled (similar to the fat liquoring in chrome tanning), dried and conditioned.

1.2.3 Post-tanning

In post tanning operation, the tanned hides are washed to remove the unfixed tanning agents.

1.2.4 Finishing

After the tanning process, the hides are processed with a series of coatings on the surface in order to improve their resistance and produce appealing and uniform surface effects. The overall objective of finishing is to
enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to (Sharphouse 1983; Sarkar 1997; UNIDO 1999): colour, gloss, handle, flex, adhesion, rub fastness, as well as other properties including extensibility, break, light and perspiration fastness, water vapour permeability and water resistance as required for the end use.

1.2.4.1 Mechanical finishing processes

A wide range of mechanical finishing operations are carried out to improve the appearance and the feel of the leather. The following list of operations includes commonly used mechanical finishing operations and conditioning (optimizing the moisture content in leather for subsequent operations)

- staking (softening and stretching of leather)
- buffing/dedusting (abrating of the leather surface and removing the resulting dust from the leather surface)
- dry milling (mechanical softening)
- polishing
- Plating/embossing (flattening or printing a pattern into the leather).

The Figure 1.1 shows the General flow diagrams of leather process steps. The water consumption in each stage of tanning processing is given in Table 1.1.
Table 1.1 Water consumption in individual operations, C: Conventional Technology; A: Advanced Technology

<table>
<thead>
<tr>
<th>Process</th>
<th>Discharge (m³/ton of raw hide processed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Soaking</td>
<td>7-9</td>
</tr>
<tr>
<td>Liming</td>
<td>9-15</td>
</tr>
<tr>
<td>Deliming/Bating</td>
<td>7-11</td>
</tr>
<tr>
<td>Tanning</td>
<td>3-5</td>
</tr>
<tr>
<td>Post Tanning</td>
<td>7-13</td>
</tr>
<tr>
<td>Finishing</td>
<td>1-3</td>
</tr>
</tbody>
</table>

Figure 1.1 General flow diagram of leather process steps
1.3 ENVIRONMENTAL IMPACTS OF TANNERY INDUSTRIES

Several key environmental issues are associated with leather processing (UNIDO 1999). It can be noticed from the above description that a large amount of wastewater is generated at various stages of tanning processing. The polluting nature of tanneries is evident from the notorious odour and the presence of unused toxic chemical in the discharge. Figure 1.2 shows the effluent generated at various stages of tanning processing. Environmentalists are more concerned with liquid effluents discharged from tanneries which contain high organic and inorganic suspended solids, high COD and potentially toxic metals.

1.4 THE CHALLENGES

1.4.1 Technical Barriers

The tanning industry is known to be very polluting especially through effluents which are high in organic and inorganic dissolved and suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues. Disagreeable odour emanating from the decomposition of protein solid waste, presence of hydrogen sulphide, ammonia and volatile organic compounds are normally associated with tanning activities. A significant part of the chemical used in the leather processing is not actually absorbed in the process but is discharged into the environment (Ates et al 1997; Kustula 2000). The wastewater from leather industries contains organics, chromium, sulphide, solid waste, buffing dust etc. Since more than 80 per cent of the organic pollution load in terms of BOD comes from early wet processing, this is the primary target of most pollution control measures. The main hurdle for adoption of environmentally
acceptable leather processing methods and effluent treatment are the cost factor and the traditional conservatism derived from hesitation over process alterations especially when satisfactory leather is being currently produced. This is more particular with small and medium sized units. In India, the tanning operations is a family business, carried out in small to medium scale semi-mechanized units and frequently grouped tightly in clusters which used to be outside residential areas. Tanners in such units have no formal education and have little or no understanding of the complexities of the leather processing, their skills acquired from their elders with hardly any perception of environmental protection. Generally speaking, tanneries in India require better skilled personnel and closer technical control than conventional processing. Thus, lack of properly trained staff at different levels remains one of the crucial constraints.

Further, the adoption of low waste technology often requires a radical alteration of most tannery processes while, at the same time, ensuring that the ultimate product retains its marketable properties. Therefore, if a tanner is producing consistent quality of leather which satisfies his customers using a process which may be wasteful in water, energy and chemical utilization, he may resist altering his operations to comply with environmental demands.
Figure 1.2 Effluent generated at various stages of tanning processing
1.4.2 Economic Barriers

It is known fact that the leather industries in India suffer from economic constraints due to increased capital or inflation rates. The escalation of chemical, machinery parts, import duties on chemicals and machinery resulted exponential investment increase in the capital cost for tannery industries. In fact this is the case with all chemical process industries, but it is obvious for small entrepreneurs.

1.4.3 Social Barriers

In addition to the economical barrier, the tanners traditionally regarded as socially inferior because of the nature of their work, makes more difficult for the government to deal with tanneries for modernization.

1.4.4 Inadequate Legislation and Lack of Monitoring Facilities

Effluent discharge standards in most developing countries are rigid and have a disregard for specific site conditions. The tanneries are under pressure to adopt an effective treatment system which can meet the norms of environmental legislation at once instead of gradual upliftment of treatment facilities, which is beyond their capacity as most of the tanneries are small and medium scale. However, this forced the tanneries to come forward with the help of government for implementing common effluent treatment plant (CETP) to meet the present challenges.

The Indian government has taken a number of steps to support the modernization of the leather industries. For example, it launched leather Technology Mission in 1995. An important objective of the Mission is to improve the environmental performance of the industry through the development and diffusion of cost effective environment friendly
technologies for the tanning industry. The Mission resulted in implementation of 170 projects at 62 locations in 16 states. The Mission is claimed to have resulted in the demonstration of cleaner tanning technologies in over 200 tanneries and microprocessor based controlled wet operations in six tanneries. It also designed and commissioned 6 CETPs for tannery clusters in South India. More recently, the government has initiated a programme providing subsidy to encourage the leather industry to modernize its production facilities. The scheme, which is administered by the Ministry of Commerce, has the following objectives:

- Replacement of obsolete machinery
- Replacement of pit technology with drums
- Installation of instrumentation and process control systems
- Promote float recycling
- In-house chrome recovery reuse facilities
- Upgradation of finishing facilities
- Promotion of non-conventional sources of energy

The scheme provides considerable subsidy of the total investment in modernization.

1.5 TREATMENT OF TANNERY INDUSTRIAL EFFLUENT

The tannery effluent is conventionally treated by physical, chemical and biological methods. The physico-chemical treatment of organic effluent consists of adsorption, coagulation, precipitation, flocculation, sedimentation, filtration, ion exchange and chemical oxidation. Coagulation has been traditionally used in tannery industry to reduce COD and suspended solids. While chromium and ammonia present in the effluent are removed through
adsorption method. The biochemical methods include biodegradation, bisorption etc. Biological methods of treating industrial effluents are suited for easily degradable organics only. However, these methods become ineffective for the effluents containing refractory (resistant to biological treatment) organic pollutants. Though the conventional methods are traditionally used in tannery industry, these methods have limitation and cannot meet the stringent norms of pollution control board standards. As a result, the industries are forced to look for alternative treatment technologies to treat the tannery effluent effectively. Among them, advanced oxidation processes have already been used for the treatment of industrial effluent containing recalcitrant organics.

1.6 SCOPE OF THE PRESENT STUDY

The objective of the present investigation is to study the feasibility of electro chemical treatment of leather effluent using electrooxidation and electrocoagulation methods. The electrochemical method is then combined with membrane process for possible improvement in membrane process. The specific objectives are

1. To treat the tannery effluent using electro oxidation, electrocoagulation


3. Optimization of electrochemical process for maximum COD removals

4. Integration of electrochemical method with membrane process.