Economic development, environmental protection, and social development are the three pillars of sustainable development. There has to be a constant balance and trade off between these three dimensions to ensure the sustainable development of any industry. Environmental protection assumes great significance because the industrial growth is sustainable only if adequate safeguards are put in place. For leather industry, this is all the more important, as all these three dimensions are intricately intertwined with one another. Leather Industry is important for India not only it has been contributing consistently to export earnings but more so due to its ability to provide employment opportunities to large number of people mainly the weaker sections of the society and women. It has been estimated that more than 2.5 million people are employed in the Indian leather industry (Taylor 2005). One of the main reasons for the development and growth of the leather industry in the country is due to its large animal population. India enjoys nearly 10% of the total global availability of raw hides and skins, which are the basic raw materials for the leather industry. The raw material availability in India as per the 2003 Raw Material Survey Report is presented in Table 1.1 (Chandramouli 2005).

India is currently producing around 2 billion sq. ft. of finished leathers and the industry has set a target to double this figure by the year 2011-12 (Raghavan 2008). On the other hand, the industry has been facing serious challenges on account of pollution related problems (Langerwerf and
Chandra Babu 1999). The presence of eco-sensitive chemicals in leathers is another area of concern (Chandra Babu et al 2005).

### Table 1.1 Availability of Hides and Skins in India

<table>
<thead>
<tr>
<th>Category</th>
<th>Pieces (in millions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle hides</td>
<td>22.770</td>
</tr>
<tr>
<td>Buffalo hides</td>
<td>27.875</td>
</tr>
<tr>
<td>Goat skins</td>
<td>81.900</td>
</tr>
<tr>
<td>Sheep skins</td>
<td>29.660</td>
</tr>
</tbody>
</table>

Though, the Indian leather industry has been able to surmount many of the challenges with huge investment being made to install pollution control devices, there are still three lingering problems, viz., compliance to Total Dissolved Solids (TDS) norm of 2100 mg/lit in treated waste waters, safe disposal of treated waster water demanding zero waste water discharge requirement and securitization of solid wastes generated (Rajamani 2007). The tannery sector in India is being compelled to comply with rigorous norms for TDS (Ramasami et al 1999). The threat of salt burden in land locked areas can lead to the leather sector being phased out of such areas. The tannery clusters may need to consider various options to reduce salt burden. It has been estimated that the salt burden on soil and water on account of tanning activity is about 0.5 million tons in terms of neutral salts (Ramanujam and Mariappan 1999). Hence, the leather industry is under close scrutiny of the environmentalists.

The means of reducing the salt in tannery waste streams include avoidance or reduction of emission of salt from soaking operation by resorting to salt-free or less salt curing methods for the preservation of skins.
and hides, modification of the leather processing methods to reduce the emission of salt and avoidance of the use of salt in processing. The necessity for the development and adoption of salt-free curing methods is gaining importance since the salt used in curing process contributes the most to the salinity in the tannery waste water.

1.1 CHEMICAL COMPOSITION AND STRUCTURE OF HIDES AND SKINS

The skin is an important organ of the body and comprises about 3-5% on the weight of the animal. The skin gives the shape to the body of the animals, protects the internal organs against abrasions and contusions, acts as barrier to the microorganisms and helps maintaining the internal body temperature. The skin is designed to keep the body cool in the summer by the evaporation of perspiration and warm in the winter by insulating against loss of body heat (Bailey 2003).

The general chemical composition and physical structure of skin is complex and varies from animal to animal (Sharphouse 1979). The freshly flayed skins and hides typically have on the weight basis about 65% of water and 30% of protein matter and the rest being contributed by fats, carbohydrates and minerals (Sarkar and Sorkar 2005). The proteins present can be broadly classified into fibrous and non-fibrous proteins.

The most important of the fibrous proteins present in skins and hides is collagen, which is the true leather making protein present in the skin. The main types of collagen in skin are types I and III (Heidemann 1993). These are known as fibrillary collagen as each collagen fibre is aggregate of many fibrils aligned parallel to one another. The amino acid composition of collagen imparts distinct characteristics of the physical, chemical and
functional properties to the protein. Collagen structure is characterized by its glycine content, one glycine at every third residue, its uniquely high proline content, often next to glycine in the sequence (-gly-pro-y-) and its unique hydroxyproline content usually next to proline in the sequence (-gly-pro-hypro-gly-) (Heidemann and Roth 1982). The presence of proline in the sequence causes the chain to twist, forming a left-handed helix. The presence of glycine at every third residue allows three $\alpha$ helices to twist together in a right handed triple helix (Ramachandran and Kartha 1955). The presence of hydroxyproline provides a powerful stabilizing effect by hydrogen bonding (Prockop et al 1979, Bansal and Ananthanarayanan 1988, Covington 1997).

Besides collagen, other fibrous proteins like elastin and reticulin are present in small quantities (McLaughlin and Theis 1924). Hair and wool present in hides and skins are made up of fibrous protein, keratin. The non-fibrous proteins include albumins, globulins, mucins and mucoids.

The lipid content of hides and skins varies from one species to another and depends on age, breed, sex, etc. Most of the lipids are contained within fat cells. Lipids may be of different types, which are triglycerides, phospholipids, cholesterol and waxes (Koppenhoefer 1938).

The skin has four distinct layers histologically and they are epidermis, grain layer or corium minor, corium major and adipose or flesh layers. The epidermis is composed of four strata of keratinous cells. The cells in layer nearest to the surface are dead and cornified and are shed constantly whereas the bottom most layer contains young cells (Bienkiewiez 1983). The epidermal layer is removed during leather processing.

The grain layer consists of fine collagen fibers and also contains major skin components including hair and related appendages, sweat and fat
glands and erector-pili muscles. This layer is also known as thermostat layer or corium minor (Datta 1999). The aesthetic value of leather comes from the grain layer.

Corium major is the main portion of the skin. It comprises a three dimensional network of collagen fiber bundles. The tightness of the weave and the average angle of weave define the properties of the skin or the leather made from it (MacLaughlin and Theis). The interweaving of collagen fibres in corium layer gives strength and resiliency to skin and leather made from it (Zapletal et al 1996).

Flesh or adipose layer is not really a part of the skin histologically. When hides and skins are removed from the animal, varying amounts of flesh adhere to different areas of the skin depending on the skill of the flayer. It is composed of fatty tissue, blood vessels, nerve and muscle tissue (Sarkar and Sorkar 2005).

1.2 PUTREFACTION OF HIDES AND SKINS

The flayed hides and skins are prone to putrefaction or bacterial degradation if left untreated. The degradation of skin is believed to begin approximately in four minutes after the death of the animal. A process called autolysis governs the onset followed by putrefaction. In autolysis, intercellular enzyme cathepsin is involved (Bienkiewiez 1983, Tancous 1970, Tancous and Jayasimhalu 1973). The various bacteria are involved in the degradation of skin. The factors that influence the degradation include temperature, humidity and degree of contamination due to dirt, blood and dung.
The process of decay does not proceed uniformly in all areas of the skin. Some skin components are more resistant to bacteria than others. The components most resistant to bacteria are fibrous proteins, collagen, elastin and hair keratin, whereas the albumins, globulin, mucoproteins, fats and soft keratin in hair root are the least resistant.

Decay starts in areas of high metabolic activity and in those containing soluble materials. Blood remaining in the veins and soft proteins in the hair follicle will be the first sites. The first visible sign of decay will therefore be a loosening of hair or wool, which is popularly known as ‘hair slip’ in tanners’ parlance (Tancous 1964, 1972, Sharphouse 1979). Fats will become softer and yellow. The attack on collagen itself will begin at the base of the hair root at the grain-corium junction causing at the worst, delamination of the grain layer and in milder cases increasing the grain looseness in the leather made from it (Tancous 1986). Nandy (1966) devised a method for the quantification of putrefaction in hides. Recently, the various aspects related to goat skin biodegradation have been studied and reported (Preethi 2006a).

1.3 FACTORS RESPONSIBLE FOR SKIN DEGRADATION

The strategy for the prevention of putrefaction should take into consideration the factors that contribute to the accelerated growth of bacteria and to device methods for controlling these factors (McLaughlin and Rockwell 1922). The fundamental requirements of most bacteria are: (a) suitable pH, (b) suitable temperature, (c) food, (d) sufficient water/moisture and (e) oxygen.
1.3.1  pH

pH is an important factor to be considered for the degradation of the skins and hides. The reason is that the bacteria or enzyme is active at neutral pH or slightly alkaline conditions. The rate of growth of damaging bacteria is most rapid around the pH of a fresh hide. It decreases at extremely high and low values. Treating hides and skins with acid or alkali would certainly reduce or eliminate bacterial activity (Guthrie and Sastry 1933). However, the effect of the treatment with acid or alkali would cause unacceptable damage to the quality of leather made from the hide or skin. These considerations and the complexity of the procedure mean that pH control is not a suitable way of preserving the fresh hides and skins.

1.3.2  Temperature

Bacterial growth is closely related to temperature. The growth is rapid in those conditions presented by a fresh hide or skin at about 37°C, which is the body temperature of the animal. It is necessary that the skin being preserved should be stored below 30°C. Most of the bacteria show considerable activity above 15°C (Mc Laughlin and Rockwell 1922, 1923). At very high temperature, bacteria would be killed. Subjecting hides and skins to high temperature would indeed stop bacterial growth but such treatment would cause irreversible changes in the substances that make leather.

Reduced temperatures below 5°C have little adverse effect on hides and skins and provide some scope for preservation. The growth of bacteria slows down or ceases at sufficiently low temperatures (Oyen 1992). But the chilling and freezing have been considered expensive processes in developing countries like India. Some more issues on these methods would be discussed in detail in subsequent sections.
1.3.3 Food

Unfortunately hide or skin, being a proteinous substrate, is an excellent food for bacteria; so nothing can be done to deprive bacteria of food except inhibiting their growth through the control of other factors. However, the growth of bacteria increases if additional food in the form of blood is available (McLaughlin and Rockwell 1923).

1.3.4 Moisture

Moisture content of the raw hide or skin is an important factor responsible for the growth of the bacteria. The moisture content of fresh hides and skins, which is about 65%, is quite adequate to support bacterial growth. However, if the water content is reduced by methods such as drying and salting, the bacterial activity decreases and eventually stops when the moisture content is less than about 35%. At this level of moisture, mould growth may still continue particularly on fatty hides and skins. The moisture content should therefore be reduced to less than 20% to provide complete preservation in the absence of any bactericide or bacteriostatic agent. If the level of water is reduced to 10% or less, two problems become apparent. First, such over-dried hides and skins become brittle and may crack during handling. Secondly, and more important, low moisture content materials rehydrate only slowly and perhaps incompletely during the course of soaking and subsequent tanning operations. Stuart and Frey (1938) reported that the growth of bacteria ceases below the critical moisture content.

The preservative action of salt is most often described in terms of its osmotic effect but a better explanation involves availability of water or $A_w$, which is the vapor pressure of the test material divided by the vapor pressure of pure water (Sweet and Hendrickson 1982). The $A_w$ of pure water
is 1 and that of hides and skins is about 0.99. Most bacteria grow best in an A_w close to that of pure water but will tolerate an A_w of 0.7. During the course of preservation procedures like salting, the high A_w of fresh hides or skins is reduced by dissolving large quantities of a soluble chemical into the moisture inside the material being preserved. The microorganisms must compete with solute molecules for the water they require for the growth (Scott 1957).

Therefore, drying makes water unavailable to bacteria physically (by eliminating some of it) and chemically (by causing an increase in the concentration of soluble materials and hence a decrease in the A_w). Salting makes the water unavailable to the bacteria physically (by eliminating some of it by osmotic effect i.e. dehydrating) and chemically (tying it up in concentrated solutions).

1.3.5 Oxygen

Some bacteria can grow rapidly without a trace of oxygen. The bacteria that require oxygen are called aerobic bacteria and the bacteria that grow in the absence of oxygen, are called anaerobic bacteria. The anaerobic digestion of skin matrix will lead to a vigorous degradation leading to the conversion of skin into amino acids.

1.4 MICROORGANISMS RESPONSIBLE FOR SKIN DEGRADATION

The main cause of biodeterioration of the raw hides and skins is due to the activity of macro- and microorganisms (Orlita 1968). Populations of microorganisms grow on raw hides mainly because of their ability to hydrolyse the proteins and lipids present. Thus proteolysis and lipolysis are responsible for the degradation of the hide substance (Orlita 2004).
There have been many studies carried out to identify the microorganisms responsible for the skin degradation (Woods et al 1970). The first microbial enzyme, collagenase, capable of degrading skin at neutral pH was isolated from the bacterium, *Clostridium histolyticum* (Harper et al 1965). Collagenase was shown to cleave the native collagen molecule into two fragments in highly specific fashion at a temperature below the denaturation temperature of the substrate. It was also shown that the cleavage takes place at a specific site closer to the C-terminal end of the molecule, yielding segments of one quarter and three quarters of the length of the native collagen molecule (Gross et al 1974, Gomez et al 1997). The active bond cleaved was Glycine-Leucine or Glycine-Isoleucine link (Bienkiewicz 1983). Tancous (1961) reported another costridum bacterium capable of causing severe hide damage and identified as probable strain of *Clostridium capitovale*. Many microorganisms were found to produce collagenolytic enzymes (Woods et al 1972, Harrington 1996, Nishimura et al 2001, Watanabe 2004,).

*Bacillus, Escherichia, Micrococcus, Proteus and Psuedomonas* were reported to be involved in the hide putrefaction (Rother, 1995). Lennox et al (1945) identified the growth of protease producing bacterial species *Proteus vulgaris* in the lamb skins during the sweating process and reported that this microorganism was responsible for hair loosening in the process.

It has been reported that *Bacillus* are the dominant bacteria involved in spoilage of hide (Venkatesan 1979, Birbir 1991, Birbir and Ilgaz 1996). Orlita (2004) also reported the presence of *Bacillus subtilis, B. megaterium, B. anthracoides, B. pumilus* on hides and skins. Gram-positive *bacilli and cocci* have been shown to dominate on non-salted cattle hides after slaughter (Hanlin et al 1995).
Ramasami (2004) reported a concerted effort to identify microflora responsible for the degradation of hides and skins. About 500-600 isolates from a sample of skin could be isolated and these isolates are expected to include also aeroflora. Number of skin microflora present seems to vary with environmental conditions from which the sample is sourced depending on season, type of animal and management protocols employed. A more detailed assessment has revealed the presence of more than 130 skin bacteria.

In a pilot study conducted with ostrich skins, microflora were isolated and identified from unsalted skins during storage and the skins were found to develop heavy growth of mixed Gram-negative *Bacilli* (Lunam and Weir, 2006). Gram-positive bacteria also colonized the skins but fewer in numbers. The Gram-positive microorganisms isolated include *Staphylococcus*, *Micrococcus* and *Bacillus* species.

An attempt has recently been made to isolate and identify the bacteria from goat skins (Ganesh Babu 2007). Most of the bacterial isolates (nineteen out of twenty one) in flayed goat skin were found to be gram positive (about 90.4%). *Bacillus* was the single dominant cultivable genus in flayed skin and it represented 71.4% of the cultivable bacterial population in the flayed goat skin. In the *Bacillus*, *Bacillus subtilis* was the dominant cultivable species and it represented 53.3% in the genus *Bacillus* and 38% in the total cultivable bacterial isolates in fresh goat skin. *Bacillus pumilus* was the second dominant bacterial species. A parallel study by Kayalvizhi et al (2008) reported the presence of several Gram-positive bacteria such as *Staphylococcus*, *Micrococcus*, *Bacillus* and *Lactobacillus* species on goat and sheep skins.

Coagulase positive *Staphylococci* were found in 39.1% of the samples collected by Desmarchelier et al (1999) in three beef slaughter
houses located in Australia. *Pseudomonas*, yeasts and moulds that are usually associated with skin, fecal material and soil occur as major contamination during slaughtering and dressing procedures (Macfaddin 2000, Doyle et al 2001, Hanson 2001).

Rangarajan et al (2003) isolated a wide variety of bacteria from the soak liquor, including species of *Bacillus, Chromobacter, Pseudomonas, Clostridium, Lactobacillus* and *Serratia marcescens*. There were also reports about the presence of *Bacillus, Clostridum, Proteus, Chromobacter, Lactobacillus, Micrococcus, Corynebacterium, Pseudomonas, Staphylococcus, Sarcina* and *Serratia* in soak liquors (Pfleiderer and Reiner 1988, Birbir and Ilgaz 1996). Venkatesan et al (1970) have studied the growth of bacteria during the pretanning operations.

### 1.5 TEMPORARY PRESERVATION OR CURING OF HIDES AND SKINS

Hides and skins are subjected to bacterial damage or putrefaction if left untreated beyond sometime. If tanneries are situated close to slaughterhouses, as it happens in some Western countries like United States of America, the leather processing can commence in green condition before the onset of putrefaction. But in most cases, the hides and skins have to be protected against bacterial damage during the period between flaying and the commencement of leather processing. The process or the treatment followed for the prevention of putrefaction is termed temporary preservation or curing. Thus a perfectly cured stock can be stored for a considerable period of time and can be transported from one place to the other until it is actually subjected to processing by the tanners.
An ideal curing procedure must not change the condition of the stock to such an extent that they cannot be brought back to their original fresh condition by simple processes like washing and soaking. The fiber structure should not be damaged physically or chemically or the inter-fibrillary proteins should not undergo any permanent change. Though, curing of hides does not come under the supervision of the tanners directly, it will have a direct influence of the quality of the resultant leathers (Koppenhoeffer and Somer 1939).

As discussed earlier, the moisture content of the raw hides and skins is a very important factor that controls the bacterial activity in them. Bacteria do not grow unless there is critical moisture content in the material (Stuart and Frey 1938). The principle of abstraction of water below this critical level is adopted in the popular curing methods.

There are two important methods of curing which work on the principle of dehydrating the skins. They are (1) simple drying and (2) salting.

1.5.1 Curing by Drying

Simplest and cheapest method of curing hides and skins is by drying them by evaporation directly under the sun. This method is prevalent in some tropical countries like certain parts of India and Africa (Marshal et al 1996). This method can be achieved in two ways: on the ground or in frames or over wires off the ground.

1.5.1.1 Flint drying

Hides and skins are spread out on the ground or on the branch of a tree and are allowed to dry out in the hot sun. As a result, the hides and skins
shrink and crumple up and are known as crumpled hides. As these hides are exposed to the hot mid-day sun, they dry out quickly forming a hard and impermeable crust on the surface, through which the moisture from the inner layer of the hides cannot come out. This leaves the inner layer wet, which may be attacked by bacteria, under suitable conditions, thus causing blisters. These are called sun ‘blisters’. This type of hides is of inferior quality (Roddy and Hermoso 1943). Pretreatment with bactericides has been attempted to prevent this. Barrett (1983) has reviewed all such efforts in a reviewed article.

1.5.1.2 Drying by pegging

It consists in stretching out the hide, flesh side up weighing it down with stones or pegging the edges with sticks to the ground. Because of the lack of air circulation from beneath, moisture and heat are retained in the hair side touching the ground, making it an extremely attractive medium for destructive bacteria.

1.5.1.3 Frame drying

In this process, the hides are stretched and dried by tying them with strings to a rectangular bamboo or wooden frame. The framed hides are then dried out in the mild sun in an open yard, where a good current of air is flowing. It is suggested that hides should be loosely suspended in frames and should not be turned according to the change in the direction of the sun rays during the day. Drying in the shade also produces good results.

Although the dried hides are practically immune to bacterial action, they are liable to be attacked and severely damaged by insects like beetles when kept in storage. Hence, such hides used to be dipped in a solution of
sodium arsenite for about a minute and then dried again. Some of the other insecticides used include D.D.T., γ-hexachlorohexane and dieldrin (Golob et al 1992).

1.5.2 Curing by Salting

There are three methods of salt curing methods practiced, namely (1) wet salting (2) dry salting and (3) brining.

1.5.2.1 Wet salting

This is the common practice followed in many countries. Hides after flaying are salted on the flesh side. Salt is generally applied in two instalments. A number of such treated hides are kept in a pile for about 10 days or more. A wet salted hide having moisture content of about 40-50% may not give problem in soaking, the first operation in leather making the moisture content of skins and hide is restored to its original moisture of about 65%.

Since sea salt often contains sulfates and chlorides of calcium and magnesium as impurities and hence, the salted skins are affected by salt stains. Salts of marine origin are also mostly contaminated with a large number of halophilic bacteria, which are responsible for the development of “red-heat” on salted hide or skin ((Jordan 1929, Bergmann 1929, Tancous 1972). To improve the salt cure and also to prevent the growth of halophilic bacteria, the use of antiseptics like sodium pentachloro phenate in admixture with salt has been advocated (Stuart and Frey 1934). However, the use of sodium pentachloro phenate has been discontinued world over as a biocide for toxicological reasons. Use of 2-4% soda ash and 1% naphthalene has also
been suggested. Boric acid is used along with salt in countries like Australia (Adminis and Money 1998).

The grain size of the salt is said to have a great influence on the quality of cure (Chandra Babu et al 2003). Normally 40-50% of salt is required on the green weight of the hide or skin for complete curing, but there is a tendency to use more salt for curing in most cases.

1.5.2.2 Dry salting

In this process, the hides and skins are first treated with powdered salt or brine and dried. The object of this method is to combine the advantages of both the wet salting and dry-cure techniques. Hides and skins are either brined or coated with brine or salted with powdered salt and then dried by nailing on boards or suspending loosely in frames. Such cured hides can be stored for longer duration and are lighter in weight. A mixture of clean salt containing 5 parts of anhydrous sodium sulphate and 1 part of sodium chloride has also been recommended for dry salting. In India, khari salt, an earthly material obtained in some districts in Bihar state is largely employed for dry salting skins. Khari salt containing mostly sulphates with a small amount of chlorides is less hygroscopic and therefore preferred for dry salting purposes over common salt (Sarkar and Sorkar 2005). Das et al (1936) compared the performance of a mixture of sodium sulphate and sodium chloride with khari salt.

1.5.2.3 Brine curing

This method is mostly followed in South America and the brine cured hides are called ‘Frigorifico’ hides (O’flaherty et al 1978).
The washed hides are put in a concentrated brine solution of about 22-24° Be for a period of 12-24 h, making sure that the hides are submerged in the brine solution. They are removed from the brine and allowed to drain. Clean fresh salt is now applied on the flesh side of each hide and the hides are piled and left in that condition for 30 days. It has been claimed that by brining, the cured hides obtained are standard cured stock that produce heavier leathers of high quality. The quality of brine cured hides against packers hides has been assessed (DeBeukeluer 1938). The brine cured hides are free from salt stains and can be preserved for a longer period (McLaughlin and Rockwell 1923). The susceptibility of brine cured hides to red heat caused by the halophilic bacteria has been investigated by Bailey and Birbir (1993, 1996).

1.5.2.4 Curing by pickling

This method is mainly used for dewooled sheepskins exported from Australia and New Zealand. Pickling preserves skins partly by dehydration and partly because of the low pH obtained in the system. Generally sulphuric acid and common salt are used for pickling skins for preservation. Either excess or insufficiency of acid or salt is harmful (Blank 1932). It has been suggested that pickle liquor should contain 12-15% (w/v) of common salt and 1.5-2.0% concentrated sulfuric acid. Fungicides are also used to prevent fungal growth (Pleass 1936).

1.6 POLLUTION PROBLEMS ASSOCIATED WITH THE SALT BASED CURING METHODS

Though there are different methods of curing followed in different situations in different countries, the most commonly used curing method is the one, which employs huge amount of common salt (40-50% on green
weight basis) for the preservation. Salt-based curing methods rely on the dehydrating and bacteriostatic properties of the salt and are very effective in preserving the hides and skins for long storage periods. The moisture content is reduced from 65% to 30% making the condition non-conducive for the bacterial growth. Further, the bacteriostatic property of salt checks the bacterial growth. Though, the method is cost effective and easy to practice, the salt curing methods suffer heavily from the environmental perspective. The soak liquor is characterized by high TDS and chloride content (Ramasami et al 1999).

Nearly 8 million tons of raw hides and skins are processed worldwide annually (Buljan 2005). Based on this figure, it can be estimated that about 3 million tons of salt are discharged during leather processing annually. The discharge of untreated spent soak liquor into land leads to significant addition of salinity to the soil (Daniels 1997). The transport of salt through ground water affects the water bodies in the region posing a major environmental challenge. Salt used in curing contributes to more than 40% TDS and about 55% chlorides in the composite tannery effluent (Kanagaraj and Chandra Babu 2002). In arid regions, TDS is turning into the main adversary of tanning industry. Tanning industry in the state of Tamil Nadu in India, land-locked regions in Australia and Italy are the examples in this regard. The effect of salinity from tanning sector on the ground water and fertility of the soil has been reviewed in detail (Daniels 2005a). The effects of the salinity on the treatment of tannery effluents and sludge have also been reviewed (Daniels 2005b). The discharge limit for TDS is quite stringent in India. In Tamil Nadu, which accounts for more than 50% of the tanning activity in India, the Tamil Nadu Pollution Control Board (TNPCB) has fixed the norm for TDS as 2100 mg/L as the state is a water-starved one (Rajamani 1998).
The TNPCB norms for the discharge of Industrial waste water are set out in Table 1.2.

### Table 1.2 TNPCB norms for the discharge of effluent

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameters</th>
<th>Discharge into Inland surface water</th>
<th>Discharge Into land for irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>5.5 – 9.0</td>
<td>5.5 – 9.0</td>
</tr>
<tr>
<td>2.</td>
<td>Total suspended solids (TSS)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>TDS</td>
<td>2100</td>
<td>2100</td>
</tr>
<tr>
<td>4.</td>
<td>BOD</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>5.</td>
<td>COD</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>6.</td>
<td>Oils and grease</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>7.</td>
<td>Chromium (Cr (III))</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>8.</td>
<td>Chromium (Cr (VI))</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>Sulphide</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>10.</td>
<td>Ammonia</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>11.</td>
<td>Chlorides</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

Note: All values except pH are expressed in mg/L.

The characteristics of the sectional and composite tannery waste water are given in Table 1.3.
Table 1.3 Characteristics of tannery waste water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Soaking</th>
<th>Liming</th>
<th>Deliming</th>
<th>Pickling</th>
<th>Vegetable Tanning</th>
<th>Chrome Tanning</th>
<th>Dyeing and Fatliquors</th>
<th>Composite (including Washing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.5-8.0</td>
<td>10.0-12.8</td>
<td>7.0-9.0</td>
<td>2.0-3.0</td>
<td>4.0-7.0</td>
<td>2.5-4.0</td>
<td>3.5-4.5</td>
<td>7.0-9.0</td>
</tr>
<tr>
<td>Bio-chemical Oxygen demand (5 days @20°C)</td>
<td>1100-2500</td>
<td>5000-10000</td>
<td>1000-3000</td>
<td>400-700</td>
<td>6000-18000</td>
<td>350-800</td>
<td>1000-2000</td>
<td>1000-3000</td>
</tr>
<tr>
<td>Chemical oxygen Demand</td>
<td>3000-55000</td>
<td>1000-25000</td>
<td>2500-7000</td>
<td>1000-3000</td>
<td>15000-40000</td>
<td>1000-2500</td>
<td>2500-7000</td>
<td>2500-8000</td>
</tr>
<tr>
<td>Total solids</td>
<td>35000-55000</td>
<td>30000-50000</td>
<td>4000-10000</td>
<td>35000-70000</td>
<td>25000-60000</td>
<td>30000-60000</td>
<td>4000-10000</td>
<td>15000-25000</td>
</tr>
<tr>
<td>Dissolved solids</td>
<td>32000-48000</td>
<td>24000-30000</td>
<td>2500-6000</td>
<td>34000-67000</td>
<td>21000-50000</td>
<td>29000-57500</td>
<td>3400-9000</td>
<td>13000-21000</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>3000-7000</td>
<td>6000-200000</td>
<td>1500-4000</td>
<td>1000-3000</td>
<td>4000-10000</td>
<td>1000-2500</td>
<td>600-1000</td>
<td>2000-4000</td>
</tr>
<tr>
<td>Chlorides</td>
<td>15000-30000</td>
<td>4000-8000</td>
<td>1000-2000</td>
<td>2000-30000</td>
<td>1000-2500</td>
<td>15000-25000</td>
<td>500-1000</td>
<td>6000-9500</td>
</tr>
<tr>
<td>Total Chromium</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2000-5000</td>
<td>-</td>
<td>100-250</td>
</tr>
</tbody>
</table>

Note: All values except pH are expressed in mg/L
The tanneries in Tamil Nadu are reeling under pressure to comply with the norms. In 1996, nearly 400 tanneries were closed in the state for non-compliance of norm for Biological Oxygen Demand (BOD) on the orders of the Apex Court of the country based on Public Interest Litigation (Kennedy 1999). Tanning Industry again faced a major crisis in the new millennium as they were asked to comply with the stringent pollution norm of 2100 mg/L for TDS. Recently, the tanneries have been ordered to install Reverse Osmosis (RO) plants to recover water from the treated waste water by the judiciary and reuse it in processing again (Rajamani 2007). Zero wastewater discharge has thus become mandatory now.

There is a tremendous pressure on the tanners to avoid the use of salts in processing or resort to in-process control measures to avoid or reduce the discharge of salt bearing streams. Salinity in the effluent are mainly contributed by the conventionally employed salt curing methods, pickling and chrome tanning operations with the major proportion coming from the common salt used in the curing process. There are attempts made to bring about process interventions such as adoption of pickle-less chrome tanning (Venba et al 1995, Munz et al 1997, Dasgupta 1998, Raghava Rao et al 2004), recycling of pickle float (Saravanan and Chandra Babu 2007) and pickle-tan closed loop chrome tanning methods (Davis and Scroggie 1973, Slabbert 1980, Sharp 1981, Arnold and Covington 1981, Chandra Babu et al 1995, Sreeram et al 2005) to minimize salt discharge from pickling and chrome tanning. But limited attention has been focused on the preservation method, which employs huge amount of the common salt. Continued use of salt cured stock without any pollution control measures for many years before the environment consciousness could take roots has given rise to degradation of land and pollution of the underground water due to high salinity in and around many of the tanning clusters in the country. In Tamil Nadu, such a situation has already led to the Loss of Ecology Authority constituted by the Supreme
Court of India slapping a fine of Rupees 380 million on the Tamil Nadu tanners to be paid to the farmers (UNIDO Report 2004). Salinity of the soil and ground water around the tanning clusters was used as the basis for the calculation of the compensation.

The current strategy to deal with the highly saline soak liquor in India can be better termed as a stop-gap arrangement and the permanent solution may rely on adopting salt-free curing methods. Hence, the need of the hour is to search and adopt cost effective and environmentally safer curing methods, which will not affect the quality of the resultant leathers adversely.

1.7 CURRENT STRATEGY FOR DEALING WITH SALT POLLUTION WITHIN TANNERIES

Currently, three basic strategies are adopted in pollution prevention and control. They are avoidance through cleaner methods, treatment at end-of-pipe and management of treated wastes in an eco-sustainable manner. TDS in tannery waste water could arise from dissolved organic and inorganic salts. They contain mostly common salt and sodium sulfate. Typical concentrations are 12000 mg/L while regulations demand 2100 mg/L in waste water (Kaul and Ravindranath 1999).

Budgeting of neutral salt found in tannery effluents indicates the following. About 50% of the common salts originate from the preservation technology used for raw material and this needs solutions at sources of raw material. 33% of salts in waste water arise from the processing technologies used in the world and this demands paradigm shift in tanning technology. 17% of salt is normally from the additions made by tanners and this demands tanner control and reduction feasible. Managing the salts residue in waste water poses challenges of technology, cost and social acceptability. Technical
feasibilities and cost viabilities in abating TDS problem in leather sector favour management options.

The salt used in curing and pickling process contributes the most to the salinity in the tannery effluents. Currently adopted strategy to deal with the spent soak liquor and pickle liquor involves the segregation of these sectional waste streams from the rest of the effluent and taking it to solar pans for evaporation to recover the salt (Kanagaraj and Chandra Babu 2002). The constraints are the space available for constructing the solar pans and the poor efficiency is due to prevailing climatic conditions. There is also additional space required now for the solar evaporation of the reject from the RO treatment methods. A novel research approach has been made to recover salt from soak liquor on laboratory scale and it has yet to be field-tested (Preethi 2006b).

The improved desalting methods prior to soaking process reduce the salinity in the soak liquor (Sahasranaman and Sampath Kumar 2001). However the disposal of the recovered salt again poses problems. The counter-current soaking method, which involves recycling of the spent soak liquor (Parthasarathi and Chandra Babu 1999, Langerwerf and Chandra Babu 1999, Raghava Rao et al 2003) reduces the soak liquor per ton of raw material considerably. This may not prove to be an effective solution if the salt is not recovered by evaporation subsequently. Moreover, there is also a problem associated with the safe disposal of the salt recovered from the solar pans. Thus the lasting solution to the problem may rest on alternative curing methods based on salt-free preservation methods.
1.8 Alternatives to Salt Based Curing Methods – A Literature Review

Due to the pollution related problems associated with the salt curing methods, many research groups all over the world are actively involved in the development of alternative curing methods. Many of these efforts have been reviewed by Hauber (1998) and Kanagaraj and Chandra Babu (2002). The various factors to be considered in the development of new curing methods are (a) bacteriological aspects of curing, (b) water content in the skins, (c) temperature, (d) humidity and (e) pH condition (McLaughlin and Rockwell 1922). Many of the attempts made are based on controlling one of these factors. Various research efforts made are discussed in this section.

1.8.1 Controlled Air Drying

The simplest and cheapest method of curing hides and skins without the use of salt is to dry them by evaporation under the sun. It is one of the eco-friendly curing processes. This method is however practicable only in countries with dry warm climate. This preservation method, where ever practiced is often poorly controlled resulting in either over drying leading to subsequent problem in further processing into leather or under drying leading to deterioration in the skin quality. Generally, the sun-dried skins produce inferior quality leathers and there are difficulties in wetting back of the skins and hides while processing into leather (Roddy and Hermoso 1943). Since, the leathers produced with sun dried stock are of inferior quality, attempts have been made to improve the curing process by resorting to controlled drying methods. The pioneering work with controlled drying have been performed by Yates (1966, 1968) and reexamined by Gratacos et al (1985, 1987, 1997). Recently, a method has been standardized for the curing of wool sheep skins in Australia (Waters et al 1997).
In the experiment conducted in Australia, the wool sheepskins were dried by controlled air drying technique using a refrigerated shipping container, the refrigerator unit of which was run in reverse cycle mode at 26°C. The container also had a refrigerated de-humidifier for controlling the humidity. In this method, a much greater control over moisture content is possible, it was shown that the skin dried this way could be stored for a long time free from putrefaction (Waters et al 1997). The rehydration during soaking was similar to that of salted skins. However, this method requires high installation and running cost.

1.8.2 Curing by Potassium Chloride

Research efforts were made to make use of potassium chloride (KCl) in place of common salt based on the assumption that the KCl will be beneficial for the growth of plants as potassium is a micronutrient. The method is very effective and the red heat is also prevented. However, the TDS problem persists and the cost of KCl is also prohibitively high. Another drawback is the dependence of solubility of KCl on the temperature; the solubility decreases with the decrease in temperature (Bailey 1994, Bailey 1995a, 1995b, Bailey and Gosselin 1996).

1.8.3 Liricure

In Liricure process developed in South Africa, the skin and hide preservation was examined using powder biocide composition. The biocides used were para-chloro meta-cresol (PCMC) and ethylenediamine tetra acetic acid (EDTA) (Russel et al 1997). The quality of the finished leathers manufactured from the sheep skins and cattle hides after the storage period of 12 months was reported to be satisfactory. A serious disadvantage of this
method is the EDTA content in Liricure powder which may cause difficulties in precipitating chromium compounds in effluent treatments.

1.8.4 Preservation by Irradiation

Attempts have been made in the United States of America (USA) to achieve hide sterilization by irradiation with gamma rays and electron beams (Dempsey et al 1965, Bailey 1997, 1999, Ross 1997, Bailey et al 2001). For hide processing, for reasons of efficacy, safety, versatility, speed and cost, electron beams were reported to be superior to gamma rays. A microprocessor controls the electron beam dose parameters of the exposure, monitoring them every one hundred milliseconds and documenting them continuously. The “dose” or measure of energy absorbed by the treated product is reproducible to within a fraction of a percent. Once the system parameters are established for a given product, the computerized control systems ensure that the process can be repeated without deviation (Vely et al 1960). The advantages of the system are the decreased salinity of effluents and there is no toxic effect. The disadvantages are: (i) the need for very expensive equipment, (ii) the need for full protection of the workers operating the equipment, (iii) possible reduction in tensile strength of the leather, (iv) the need for covering each hide with plastic bags to prevent recontamination with microorganism during storage and (v) high cost of treatment (Russell et al 1982).

1.8.5 Curing by Silica Gel

In place of the salt which functions as a curing agent mainly because of its ability to dehydrate the hide/skin below critical moisture content apart from its bacteriostatic property, a dehydrant silica gel has been used to preserve the raw hide/skin alone or with reduced offer level (5%) or in combination with a preservative (Kanagaraj 1999, Kanagaraj et al 2000,
2001). The efficacy of the systems were analyzed by the moisture content, total extractable nitrogen content, bacterial count and pollution load generated during leather processing. The results showed that the leather obtained was comparable in properties with a potential to reduce pollution load in terms of TDS by 70-75% and chlorides by 80-85 percent compared to salt curing system. Recently, neutralized silicate formulation has been successfully exploited for the preservation of skins and hides in Indian subcontinent and in Europe (Munz et al 2006).

1.8.6 Other Reported Curing Methods

Earlier work on short term preservation of hides at Eastern Regional Research Laboratory in USA was directed towards the use of benzalkonium chloride (BAC). BAC has been tested for the short time preservation of hides and skins (Cordon et al 1964, Benrud 1969). The percentage of BAC used for the preservation of fresh calfskin ranged from 0.1-0.4 percent. There was no difficulty in processing hides treated with this material and no adverse effect on the leather was found. Other studies have also confirmed the effectiveness of BAC (Sivaparvathy and Nandy 1974, Russell and Galloway 1980). Another quaternary compound, cetyltrimmonium bromide has also been successfully screened for the curing of goatskins recently (Ganesh Babu et al 2007).

Temporary preservation of hides using a saturated aqueous solution of boric acid was attempted successfully in New Zealand (Hughes 1974). Hides soaked in saturated boric acid solution had storage life of only 15 days. Studies carried out in South Africa (Sladen 1977), The Gambia (Barret 1983) and India (Kanagaraj et al 2005) also confirmed the usefulness of boric acid for preservation.
It has been found that the wide range of materials, both organic and inorganic compounds can be used for the preservation of skin/hide in combination with common salt (Venkatachalam et al 1982). The use of sodium chlorite, sodium carbonate, propionic acid and peracetic acid as well as organic antiseptic reagents such as teborit and hyamine for curing has also been reported.

Short term preservation with aryl alcohol has been reported (Venkatachalam et al 1981). It was found that aryl alcohol at a total dosage of around 2-3% (on green weight) gave satisfactory preservation for about two months. It was also found that hypo at the level of 5% was able to preserve the buffalo hide and goat skin for 10 days. The zinc sulphate at the level of 5% and a mixture of benzaldehyde (0.5 per cent) with B-naphthol (0.5 percent) could also preserve the stock for 3 days and 1 week respectively.

Preservation of skin by using sulphites, bisulphites and meta bisulphites in conjunction with an acid has also been reported (Hopkins and Bailey 1975, Bailey and Hopkins 1975, Bailey et al 1976). The reactions of these reducing agents with acid produces sulphur dioxide which bring about resistance to bacterial degradation. Studies were also carried out using sulphur dioxide gas (Hopkins et al 1973, Hopkins 1980, 1983, Hopkins and Bailey 1981). While this process is effective, its major disadvantage is the high human toxicity of sulphur dioxide released by the hides.

A systematic screening and evaluation of preservatives for skin preservation was carried out at CLRI by studying their inhibitory action against certain strains of bacteria (Sivaparvathy and Nandy 1974, Sivaparvathy et al 1993).
The development of salt-less preservation by the use of the neem oil with alcohol has also been reported (Krishnamurthy et al 1977). The neem extracts were applied to both flesh and hair sides at about 1% on the green weight. After the treatment, the experimental skins were allowed to dry in the shade. The skins, by this method can be preserved for more than 6 months. But the resultant leathers were of inferior quality. Recently, an attempt has been made to use neem leaf paste for curing of skins and hides at ambient conditions (Preethi et al 2006c).

Joseph et al (1982) had reported the use of non-steroidal anti-inflammatory drugs for the preservation of goat skins. Preservation of skins by using Bronidiol was also reported (Rao and Nandy 1982). Use of antibiotics to control green hide biodegradation has been also reported, where the effects of aureomycin, terramycin, chloromycetin, tetracycline and streptomycine have been examined (Berwick et al 1996).

A short term preservation technique for the cattle hides using a combination of sodium chloride and hydrolyzed starch-poly acrylonitrile graft co-polymers after washing with 4 percent acetic acid has been reported. The approach made is based on the principle that by regulating water activity to maintain micro bio-static conditions to produce a quality hides with minimum handling processing and storage. This method of short term preservation depends on control of Gram positive micrococi and bacilli and there was no sign of bacterial or mold growth after 11 weeks of storage (Sweet and Henrickson 1982).

The preservation of hides and skins by taxidermists approach, where the living shape of an animal was recreated in a relatively permanent condition often, illustrative of the characteristics of the living animal (Reid 1982). This was done using various chemicals including mercury, bichromate,
alum, borax, boric acid and phenol derivatives, but toxicity of many of these chemicals is questionable.

For the short term preservation of hides, a Zimbabwean method based on chilling and treatment with bactericides such as benzalkonium chloride, boric acid, a polymeric biguanidine hydrochloride, 2(Thiocyano methyl thio-benzothiazole) (TCMTB) and a mixture of sodium 2-mercaptop benzothiazole and potassium hydroxy-N-methyl dithiocarbamate have been reported to yield better results in comparison with conventional salt cured method (Haffner and Haines 1975).

Another short term preservation of cattle hide using 20% soda ash solution (w/v) has also been reported (Rao and Henrickson 1983).

For the short term preservation of hides, the use of chlorites and hypochlorites has been examined (George and Krishnamurthy 1966, Money 1970, 1974, Cutting and Scroggie 1971, Haffner and Haines 1975, Cooper and Galloway 1980) but there is a potential hazard associated with the use of chlorite.

Hopkins et al (1973) defined the short term preservation as ‘that period of preservation extending from hide removal to seven days’ and also compared the performance of various techniques for hide preservation.

1.8.7 Chilling and Freezing

Chilling and freezing are practiced universally for preservation of meat but only in Western countries and Australia, industrial application of cooling system for hides and skins is being practiced to a limited extent. Hausum (1939) in his reviews described early experiments on cold storage of hides and skins mainly in relationship to salted raw stock. He also reported
that hide freezing has been a common practice in colder regions of erstwhile Soviet Union. Frey and Stuart (1941) have done a systematic study on the cold storage for salted calf skins. A pretreatment with a biocide followed by chilling has been studied for the storage of ostrich skins in Africa (Cooper 2001). Balas (1985) and Gavend and Rabbia (1986) have also experimented with curing using cold storage.

In Australia, studies were conducted for freeze curing of hides for long term storage and it was estimated that cost savings to the tune of 30% in comparison with salt curing was possible. Now it is commercial practice in Australia to use chilling as a method of short term preservation for hides for certain situations (Adminis and Money 2003). A temperature between 2 and 5°C is employed and the results are reported to be satisfactory. However, preservation time is limited and Table 1.4 summarizes the dependence of preservation time on the storage temperature.

**Table 1.4 Dependence of preservation time on chilling temperature**

<table>
<thead>
<tr>
<th>Preservation temperature °C</th>
<th>Preservation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3 weeks</td>
</tr>
<tr>
<td>5</td>
<td>2 weeks</td>
</tr>
<tr>
<td>10</td>
<td>5 days</td>
</tr>
<tr>
<td>15</td>
<td>2 days</td>
</tr>
<tr>
<td>20</td>
<td>1 day</td>
</tr>
</tbody>
</table>

Extensive studies were conducted in England to compare the leather making qualities of frozen and salted hides (Haines 1981). Studies at British Leather Manufacturers’ Research Association demonstrated that chilling hides rapidly after flaying and holding at –1°C would allow hides to remain in satisfactory condition for three weeks (Haffner and Haines 1975).
Chilling was practiced in some hide markets in the United Kingdom during seventies (Barrett 1986).

The quality of the preservation depends on the temperature during the transfer period. Cooled hides and skins should be kept in a well-insulated or refrigerated storage to get the best results. In practice, one of the following methods is adopted to bring about refrigeration of the skins and hides (Oyen 1992).

(i) Cooled air treatment
(ii) Addition of ice
(iii) Carbonic dry ice addition

1.8.7.1 Cooled air treatment

This technology was adapted to large slaughterhouse, where it was possible to automate and therefore cool and store large quantities of hides without handling (Hausum 1939). By this technique it was possible to process 300 hides/h on a continuous conveyor. Hides were cooled at 5° C for about 45 min. It has been reported that in Australia, the skins preserved this way after storage for 5 days are transported to a wet blue tannery about 700 km away. A company in Germany is processing 70 per cent of its production with cooled air. The hides after flaying are cooled at 3° C and piled on palettes. In the case of hot weather, some ice is added between the hides. The use of conveyor during the cooling process helps to improve the thermal exchange on hanged hides.

1.8.7.2 Addition of ice

It was possible to cool hides and skins in a continuous way in a mixer by using some ice cubes, cakes or flakes, just after flaying. It is also
possible to put hides or skins in a cooled tank and then to add some ice in the storage container, within 2 h, hides are cooled from 30 to 10° C and can be stored for 24 h without further treatment. This method is being followed on large-scale in Switzerland, Germany and Austria. The cost of an ice-making machine is low compared to a cold room investment. The British Leather Confederation has further improved this technology by the use of preservative solution to produce ice. The limitation of the process is the draining of liquor containing high concentration of preservative (BLC 1992).

In Ireland, a new liquid-ice raw hide preservation was commercially introduced (Hodges 2002).

1.8.7.3 Use of dry ice

The concept of cooling lamb or sheepskins with dry ice for short term holding and transportation was researched in United Kingdom and New Zealand (Daniels 1995). Compared to the normal ice, the hides and skins are cooled to -35° C and cooling is achieved rapidly in the whole area of skin/hide. The method does not suffer from the problems normally associated with the use of ice, such as re-wetting problem and brine draining from melting of normal ice. It gives a uniform cooling and preserves the hides or skins for a minimum of 48 h.

However, special care has to be taken because of the suffocation risks by the use of carbon dioxide. The cold conditions and the high pressure of carbon dioxide storage must be taken into account. Dry ice used was estimated to be 60 g/kg of hide, corresponding to 15 L of gaseous carbon dioxide. This type of processing seems much more adopted for skins that keep the temperature longer than hides. Haines (1981) compared the advantages and disadvantages of each technology.
Advantages of chilling in comparison with freezing include lower energy costs and there is no problem of having to thaw the hides at the tannery. Some times, the tissue fibers might be damaged during freezing and therefore, it was reported to be unreliable. It was also reported that at the end of the freezing period, the bacterial degradation was faster than with the cooled hides. Any hindrance in the freezing step might promote bacterial growth. The other disadvantages are the high investment and operation costs and high power consumption, especially in warm climates and higher slipperiness of the pelt during fleshing.

In conclusion, it appears worthwhile to investigate further the technical and commercial feasibility of chilling in Indian conditions for the short term preservation.

1.9 CHILLING AS AN ALTERNATIVE SHORT TERM PRESERVATION OPTION AND THE NEED FOR THE PRESENT STUDY

Chilling as a method of preservation is a good alternative to salt preservation, as there is no pollution, no contamination of by-products, it is suitable for all hides and skins and there is no hair-loosening. The temperature at which hides and skins should be chilled depends on the required time of preservation.

Chilling is popular as a method of short term preservation in the developed countries including Australia for situations, where the chilled hides from slaughter house/abattoirs can be transported in insulated containers by overnight journey (Adminis and Money 1998). But Chilling is usually not considered an option for Indian situations for various reasons. In India, the slaughtering of animals and collection of hides are done in a decentralized
way. There are a very few large, organized slaughterhouses /abattoirs in India and are mostly confined to some metropolitan cities. Moreover, the chilling systems are generally considered expensive. But according to the information available, chilling method of curing may not be unsuitably expensive in India. However, this method can work only in situations, where the tanneries are directly sourcing the raw skins and hides from the slaughter houses or primary collection centers and the distance of transportation is less than 8 hours drive. There are such situations available in India and one of the classical examples is the Erode Wet blue tanning cluster sourcing cow hides from important raw hides markets in Kerala.

The chilling as a method of preservation may prove quite economical when applied to large scale production in tanneries. The chilling is achieved in a unit, where very low temperature is maintained. This option is being widely used in many countries totally based on the conventional knowledge available to them and no systematic detailed study encompassing all the issues has been done or reported in this respect. Moreover, in India, since the raw material collection is very much decentralized, the standardization of a suitable chilling method suited to collection system in the country on one hand and the aero-flora involved in skin putrefaction in a tropical climatic condition on the other require the scientific input on these critical aspects. Hence, the present investigation has aimed at a systematic study of all the issues involved in such a curing method such as microbiological aspects, optimization of chilling temperature, study on the chilling profile to optimize the rate of chilling and study of thawing profiles to optimize the duration of storage or transportation in an insulated container or the truck as well as technology aspects by studying in details the various changes taking place during preservation of hides and skins while chilling and to come up with a cost effective optimized method of preservation of skins and hides suitable to Indian conditions.
1.10 SCOPE OF THE WORK

Due to the stringent pollution control norm for TDS and salinity in tannery effluents in India, there is a need to develop and adopt salt-free curing methods suitable for Indian raw material supply chain system. Chilling is the most commonly employed short term preservation method in many countries and is considered more efficient and cost effective than biocides based methods. There is a need for a study aimed at the rationalization of the chilling method in Indian context so as to standardize a suitable system and hence such an attempt has been made in this investigation. The main scope of the present investigation has been identified as to

- Optimize the chilling temperature for the preservation of cow hides by studying the growth profile of skin putrefying microorganisms at different low temperatures
- Study the effect of different chilling temperatures on the curing efficacy as well as on the structure of the cured skins and hides and on the quality of the leathers by carrying out laboratory scale experiments in a refrigerator cabin
- Study the chilling profile for the hides to optimize the rate of chilling so that temperature of the hide can be brought down before the onset of putrefaction
- Study the chilling and thawing profiles of the cow and buffalo hides on larger scale using the mobile chiller designed and fabricated for the purpose
- Study the rate of degradation during the thawing of the chilled hides by the bacterial count in the hides and release of ammonia, and tyrosine and hydroxyproline from the hides to
decide about the duration of storage or transportation in insulated container

- Study the effect of the optimized chilling method on the quality, strength and structural properties of leathers produced on large scale

- Estimate the cost benefit analysis for the chilling method of preservation vis-à-vis salt method of preservation to assess the commercial viability under Indian conditions and

- Develop a technology package based on chilling method of preservation for the implementation of region-specific (in this case India) cleaner curing system.