CHAPTER 1

INTRODUCTION

1.1 LEATHER INDUSTRY : AN INTRODUCTION

Leather industry is an age old industry and has been serving the society as an important consumer industry. It provides a wide range of consumer goods such as shoes, garments, bags etc. However the tanning industry has been categorised as one of the highly polluting industries and there are concerns that leather making activity can have adverse impact on the environment. The global production of about 24 billion sq. meters of leather by the year 2005 presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing. The tannery effluents are characterised by high contents of dissolved, suspended organic and inorganic solids giving rise to high oxygen demand and potentially toxic metal salts and chromium metal ion. The disagreeable odour emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia and other volatile organic compounds is also associated with tanning activities.

The last two decades have witnessed substantial relocation of leather making activity from industrialised countries to the developing countries on account of high cost of effluent treatment installations and treatment methods. However, in the recent times, leather industries in the developing countries are
also facing threat of closure due to court orders based on public interest litigations. An increased public awareness leading to stricter enforcement of pollution control regulations has forced the leather industries in these countries to adopt cleaner leather processing methods in the recent times.

1.2 LEATHER INDUSTRY : CURRENT STATUS

The raw material for leather industry is the raw hide or skin. It is subjected to a wide range of pH alterations. It involves the use of copious amounts of water. Environmental challenges from leather processing arise from the nature and quantum of chemicals used as well as the amount of wastes generated and discharged.

The salt used for preserving the skin/hide discharges huge amount of pollution load in terms of Total Dissolved Solids (TDS) and chlorides. Other major polluting chemicals used in tanning industry which cause pollution are lime, sodium sulphide, ammonium salts, sulphuric acid, chromium salts and vegetable tanning materials. Typical emission factors expressed as wastes generated for every tonne of leather processed at various stages of processing are presented in Table 1.1 (Ramasami et al 1999).

Typical values of utilisation of chemicals in leather processing are indicated in Figure 1.1 (Ramasami et al 1999a).
Table 1.1  Typical Waste Emission Factors Associated with Leather Processing

<table>
<thead>
<tr>
<th></th>
<th>Soaking</th>
<th>Liming</th>
<th>Deliming</th>
<th>Pickling</th>
<th>Chrome Tanning</th>
<th>Dyeing &amp; Fatliquoring</th>
<th>Composite (incl. Washing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅</td>
<td>8.3 - 18.8</td>
<td>17.5 - 35.0</td>
<td>1.5 - 4.5</td>
<td>0.3 - 0.5</td>
<td>0.5 - 1.2</td>
<td>1.5 - 3.0</td>
<td>35.0 - 105.0</td>
</tr>
<tr>
<td>COD</td>
<td>22.5 - 45.0</td>
<td>35.0 - 87.5</td>
<td>3.8 - 10.5</td>
<td>0.8 - 2.3</td>
<td>1.5 - 3.8</td>
<td>3.8 - 10.5</td>
<td>87.5 - 280.0</td>
</tr>
<tr>
<td>Total Solids</td>
<td>262.5 - 415.5</td>
<td>105.0 - 175.0</td>
<td>6.0 - 15.0</td>
<td>26.3 - 52.6</td>
<td>45.0 - 90.0</td>
<td>6.0 - 15.0</td>
<td>528.0 - 875.0</td>
</tr>
<tr>
<td>Solids suspended</td>
<td>22.5 - 52.5</td>
<td>21.0 - 70.0</td>
<td>2.3 - 6.0</td>
<td>0.8 - 2.3</td>
<td>1.5 - 3.8</td>
<td>0.9 - 1.5</td>
<td>70.0 - 140.0</td>
</tr>
<tr>
<td>Solids chlorides as Cl⁻</td>
<td>112.5 - 225.0</td>
<td>14.0 - 28.0</td>
<td>1.5 - 3.0</td>
<td>1.5 - 3.8</td>
<td>23.0 - 38.0</td>
<td>0.8 - 1.5</td>
<td>210.0 - 332.5</td>
</tr>
<tr>
<td>Chromium (total) as Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.0 - 7.5</td>
<td>-</td>
<td>3.5 - 8.8</td>
</tr>
</tbody>
</table>

(All values expressed in kg/tonne of hide processed).
1.3 ENVIRONMENTAL ISSUES

1.3.1 Water Pollution

Currently about 6.5 million tons of wet salted hides and skins are processed worldwide annually. Based on this figure, it is estimated that about 3.5 million tons of various chemicals are used for leather processing. A considerable part of this amount is not taken up by the hide/skin during the process and is discharged into the effluent. At an average consumption of 45-50 cubic metres of the waste liquor per tonne of raw hide, over 300 million cubic meters of waste liquor containing thousands of tons of chemicals and solid waste are discharged by the leather industry. They are to be treated
adequately and disposed scientifically complying with the statutory requirements. The composition of liquid and solid wastes generated in tanneries worldwide are presented in Table 1.2 (Ludvik 1995).

Table 1.2 Composition of liquid and solid wastes generated in tanneries worldwide

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Tons (in thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Oxygen Demand</td>
<td>1470</td>
</tr>
<tr>
<td>Biochemical Oxygen Demand</td>
<td>610</td>
</tr>
<tr>
<td>Suspended Solids</td>
<td>920</td>
</tr>
<tr>
<td>Chromium</td>
<td>30</td>
</tr>
<tr>
<td>Sulphide</td>
<td>60</td>
</tr>
<tr>
<td>Solid Wastes (Trimming, fleshing, shaving and buffing dust)</td>
<td>3000</td>
</tr>
</tbody>
</table>

The characteristics of the tannery wastewater are complex. They vary in strength from tannery to tannery and region to region. The principles involved in these processes are same at every centre. In addition, the intensity of pollution is related to the quality of raw materials including the hides and skins and other ancillary chemicals with reference to geographical location. It is observed that tannery wastes are stronger than sewage and far different in constituent pollutants. For example, chromium, sulphides and total dissolved solids are unique to tannery wastewater.
1.3.2 Soil Pollution

The impact of tannery wastewater on water bodies has been studied extensively. Salination of water is the primary concern that affects plant kingdom (from flora, fauna to fertile trees) and ground soil. It is a serious concern to the regions which depend largely on ground water.

The untreated wastewaters from tanneries have been applied on land merely to contain them at one place. The long-term use of land for disposal of wastes has resulted in contamination of soil. The soils holding it directly and irrigated with contaminated groundwater have been reported to lose productivity (Mariappan 1997).

1.3.3 Atmospheric Pollution

The tanneries are proverbially known for generating malodor. The rehydration of salted hides and skins generally emit odor of volatile fatty and amino acids evolved in the course of biological decomposition in the presence of water. In addition, the stench of hydrogen sulphide along with acids, fats, carbohydrates etc. in liming, deliming and tanning processes is predominant within the tanneries. The venting out of malodorous substances to ambient air and subsequent transports to further distance are responsible for atmospheric pollution. Hydrogen sulphide at 20 ppm (30 mg/m$^3$) in ambient air is lethal to human kind.

Ammonia escaping from deliming operation to atmosphere is odorous and pungent. It is equally hazardous to human kind. The maximum admissible level of ammonia in air is 50 mg/m$^3$. 
The phenolics (monohydric, dihydric and trihydric) are emitted into air during the processing of hides in the post-tanning and finishing operations. The permissible level of phenolics as phenol (C$_6$H$_5$OH) in water is 10.2 mg/l. The concentration shall not exceed 0.3 mg/l in drinking water. The toxicity of sulphide, ammonia, phenol and chromium that are found in tannery wastewater to freshwater fish has been reported (Mariappan 1997). They recommended the need to dilute the raw wastewater to 100-150 times with freshwater in order to prevent the damage to fish. The impact of tannery effluent on micro and macrophytes has been studied. The germination of seed is severely affected and the growth of plants retarded significantly.

1.4 SKIN COLLAGEN AND SOLID WASTES

1.4.1 Skin Collagen

Animal skin, like other tissues of the body, is composed of proteins, lipids, carbohydrates, mineral salts and water. The solid matter of the skin is made up of 90-95 percent of proteins. In the whole fresh skin, they comprise roughly 35 percent of the weight. Several classes of proteins are present, the most important of which are collagen, elastin, keratin, glycoproteins, albumins and globulins. Among these, collagen is the most important protein in the skin because it is present in the largest amount and is responsible for the formation of leather by combination with tanning agents (Ramasami 2001). It is one of the fibrous proteins and constitutes approximately 30-33 percent of the weight of the whole fresh skin. Histologically the skin is divided into three layers (i) Epidermis, (ii) Corium and (iii) Flesh or Adipose tissue. Epidermis constitutes only 5% of the total skin, and the chief constituent is keratin, whereas corium constitutes collagen, the most important protein from the leather making point of view. The structure of collagen is represented in Figure 1.2.
The collagen fibres are enclosed in a connective tissue known as sarcolemma. It is insoluble in water and in dilute solution of acids and alkalies and in organic solvents at ordinary temperatures (McLaughlin and Theis 1945). It possesses greater amount of swelling property in aqueous, acid and alkaline systems in absence of salt concentration. The basic structure of collagen is triple-helical chain. The helix has three chains, each being a left-handed helix itself with three residues per turn (about 1.0 nm). The important features of the collagen is three α chains with a repeating Gly-X-Y sequence staggered by one residue relative to one another (Ramachandran and Kartha 1954). The amino acid composition of collagen shows distinct characteristics of the physical, chemical and functional properties of the collagen. Collagen is characterised by its high glycine content (33%), one glycine at every third residue. There is an absolute requirement for glycine in every third position, since glycine is the only amino acid with no side chain. The imino acids, proline and hydroxy proline content are 22% of the overall amino acids. The ring structure of imino acids prevents rotation about the N-Cα bond in a polypeptide chain. In addition, model studies and energy calculation show that rotation about Cα-C=O bond is

Figure 1.2 Molecular structure of collagen

- Glycine
- Predominantly imino acids
restricted. Proline and hydroxyproline is therefore a major element in stabilizing the confirmation. In collagen, any amino acid can precede or follow glycine in the X and Y positions. In practice some preferences have been observed. Glutamic acid, histidine, leucine, and phenyl alanine are usually in the X position, while threonine, lysine and arginine are usually in the Y position. Proline would be equally distributed but when it precedes glycine it is usually hydroxylated to 4-hydroxyproline after translation. Water molecules can be fitted into the structure in various ways. Two hydrogen-bonded water bridge per triplet from the hydroxy group of hydroxyproline to a backbone carbonyl oxygen has been suggested (Ramachandran 1967).

Apart from collagen, fleshing is also present in the skin. Varying amounts of fatty adipose tissue, blood vessels, nerves and voluntary muscles constitute fleshing. It is removed during liming operation of leather processing.

1.4.2 Solid Wastes

Several researchers are carrying out study in solid wastes for the reduction of pollution problem in leather processing. The tannery generates huge amount of fleshing as a solid waste. The Table 1.3 shows environmental balance of leather production.
Table 1.3 Environmental Balance of Leather Production

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Material generated</th>
<th>Kg/tonne of raw skin / hide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Leather</td>
<td>150</td>
</tr>
<tr>
<td>2.</td>
<td>Solid waste (Skin trimming, fleshing, buffing, chrome shaving wastes)</td>
<td>850</td>
</tr>
<tr>
<td>3.</td>
<td>Fleshing</td>
<td>400</td>
</tr>
</tbody>
</table>

Thus, out of 1000 kg of raw hide, nearly 850 kg of the raw material is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather.

The solid wastes in the leather processing constitute 80% from beam house, 19% from tanning and 1% from finishing. The solid wastes can be hydrolysed and used as a useful by product in many ways. The Figure 1.3 shows the flow diagram of various ways of hydrolysis and utilising the solid wastes (Post 1997).

Table 1.4 shows the percentage of various solid wastes generated in the leather industry (Ludvik 1995).
Figure 1.3 Flow diagram of solid wastes utilisation
<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Types of solid wastes generated</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hair</td>
<td>2 – 5%</td>
</tr>
<tr>
<td>2.</td>
<td>Fleshing</td>
<td>50 – 60%</td>
</tr>
<tr>
<td>3.</td>
<td>Chrome shavings, chrome splits and buffing dust</td>
<td>35 – 40%</td>
</tr>
<tr>
<td>4.</td>
<td>Skin trimmings</td>
<td>5 – 7%</td>
</tr>
</tbody>
</table>

Several technologies have been explored for the utilisation of solid wastes generated in leather industry. Among the solid wastes keratin plays an important role because of the difficulty in hydrolysing it. The disulfide bond plays an important role in safeguarding the keratin. It is highly resistant towards enzymes and most of the chemicals. It is rich in cystine containing amino acids.

**1.4.2.1 Keratin wastes**

Keratin has been hydrolysed by using strong alkali such as sodium hydroxide and hydrochloric acid. The hydrolysate prepared from keratinous material has been employed in chrome tanning and rechroming at various levels and the exhaustion is studied. The study showed that the hydrolysate helps to improve the chrome exhaustion of tanning bath and rechroming bath. The physical strength properties are also not altered (Ramamoorthy et al 1989).

**1.4.2.2 Fleshing wastes**

Modified fleshing hydrolysate has been prepared from fleshing and acrylic acid. The resultant product has been used as an aid in chrome tanning
and in rechroming. Modified fleshing hydrolysate at the level of 2% showed improved uptake of chromium in chrome tanning and rechroming. The physical strength properties and organo-leptic properties of leather are better than conventionally produced leather (Kanagaraj et al. 2002).

1.4.2.3 Chrome shaving wastes

Chrome tanned leather, splits and trimmings have also been found to be useful by product. These solid wastes have been useful in obtaining glue, gelatin, protein flavour and reconstituted collagen. The above products can be made by treating with hydrogen peroxide to bring about important degree of maceration and then grinding and extraction to yield the by-product in the order of 95% (Cot et al. 1986).

Chrome shaving has also been hydrolysed by many ways. Various alkalinity-inducing agents, such as magnesium oxide, alone or in combination with calcium hydroxide or sodium carbonate have been employed to maintain the optimal environment for enzyme hydrolysis. It has been shown that magnesium oxide alone in combination with calcium hydroxide, sodium hydroxide or sodium carbonate will increase the efficiency of the solubilization and at the same time reduce the amount of enzyme needed and thus making the treatment more cost effective (Taylor et al. 1991). Land application and disposal of chromium containing tannery wastes into a useful means have been discussed. The results showed that chromium containing leather and product wastes poses little or no environmental hazard. There is no migration of Cr(III) at actual land disposal sites (Rutland 1991). Similarly chrome tanned hide collagen in the form of trim, splits and shavings have been converted into glue.
Economics including the cost of raw materials and the yield of protein have been achieved in a better way (Pearson 1981).

Wet blue trimmings, shavings, buffing dust and trimming from crust and finished leather have been converted into glue, feed and fertilizers. Some of the wastes have also been converted into landfill sites (Lollar 1981).

Gels, adhesives and films of high molecular weight gelable protein fraction have been obtained from chrome shavings under mild alkaline conditions. However, the characteristics of the products depend on the composition of the original chromium waste product and on the specific treatment conditions (Brown et al 1994; Brown et al 1996).

Chrome shavings have been treated with proteolytic enzyme at a temperature from 60-65°C in the presence of 5-6% lime. From this, protein present has been separated by filtration leaving chromium cake. The protein hydrolysate containing less than 4.5 ppm chromium is potential as a feed, fertilizer, or as an additive in the cosmetic industry (Taylor et al 1990).

The interaction of gelatin and polyphenols has been studied (He Xianqi et al 1994). The relation between molecular structure of polyphenols and their hydrophobicity has been investigated. The results showed that galloyl and polyphenols had hydrophobic sites. Then polyphenol-amino acid and polyphenol-gelatin interactions showed that hydrophobic association between gelloyl groups of polyphenols and hydrophobic position of gelatins had predominant pattern of polyphenol-gelatin interaction.
Gelable and hydrolysed protein products from chromium containing leather waste have been obtained by using various alkali inducing agents. Magnesium oxide (MgO), carbonates and hydroxides have been used to obtain the product compared to the use of MgO alone; the use of MgO in combination with sodium or potassium hydroxide increases the chromium content of the hydrolyzed protein products. Carbonates and hydroxides have a detrimental effect whereas MgO has the most significant effect (Taylor et al 1994).

The use of hydrolysate from chrome-tanned wastes for producing biodegradable plastic particularly applicable in agriculture for the breakdown of synthetic polymers has been studied. It has been confirmed that protein hydrolysate from chrome shavings markedly increases biodegradation of material and also exerts a positive influence on mechanical properties (Kresalkova et al 2002).

Films of high quality have been made from commercial gelatins. Commercial gelatins have been enzymatically treated with a microbial transglutaminase mixed with glycerol as plasticizer. The results showed that the amount of glycerol added affected the mechanical properties, particularly the maximum strain. Increasing the concentration of crosslinking agent gave products with higher tensile strength and improved water absorption properties (Taylor et al 2002).

Chrome shavings have been used for making chrome cakes. Characterisations of the chrome cakes and the protein generated by these methods have been studied. The unwashed chrome cakes showed moisture content of 83.9%, ash 40.57%, Total Kjeldahl Nitrogen (TKN), 6.07%, Chromium content (Cr₂O₃), 4.2% (Taylor et al 1992).
Chrome shavings have been used to obtain gelatin. These shavings have been treated with enzymic solution pepsin A (3900 units/mg), trypsin (10, 400 units/mg) for 6-24 hours at the optimum pH of 8 and gelatin has been extracted at 70°C. The results showed that pepsin behaves as a mild-enzyme with a controllable effect on leather wastes and trypsin gave a better yield (Cabeza 1997).

Solid wastes such as lime fleshing and chrome shavings have been hydrolysed by Paecilomuces litacinus. The effectiveness of the hydrolysis has been determined by kjeldahl nitrogen analysis. The result showed that the rate of fleshing hydrolysis is 93% in comparison with conventionally hydrolysed fleshing of 87% (Chakraborty and Sarkar 1998).

Utilisation of chrome shavings and improved penetration as well as adequate exhaustion of chrome liquors in chrome tanning process has been studied. Shavings containing about 2% Cr₂O₃ have been hydrolysed with sulphuric acid and the resultant hydrolysate has been added in different amounts to commercial chrome tanning salts for carrying out chrome tanning process (Manzo et al 1993).

Chrome shavings have been treated with pepsin-trypsin and pepsin-alkaline protease and various products such as gelatin, chrome cake and hydrolysate have been prepared. The shavings have been pretreated with pepsin at room temperature and gelatin has been extracted with water at 70°C. The chrome sludge recovered after centrifugation has been treated with trypsin or alkaline protease and hydrolysate has been extracted at 70°C. The chemical properties showed that high quality of gelatin is produced by these method (Cabeza et al 1998; Cebeza et al 1998a).
Chrome shavings have been pretreated at 67-69°C with anionic surfactant in water (500% float) for 2 hrs. Pretreatment with MgO to maintain the pH and alcolase (Novo Nordisk) 345 ml has been added and left for 3 hours. After the enzyme digestion high quality of getable and protein products have been obtained from chromium containing leather waste (Taylor et al 1997).

Alkaline hydrolysis assisted by proteolytic enzyme at moderate temperature of 55°C for the chrome tanned leather had resulted in collagen hydrolysate, chrome cake and chrome (III) tanning salts. Application of collagen hydrolysate in retanning process and chromium tanning salts in tanning and retanning gave good quality of leather (Cantera et al 1997; Cantera et al 2003).

Pilot plant trials of a process to treat chrome shavings to isolate protein products and purified chromium have been studied. The chemical and physical properties showed that the extracts of gelatin with alkali gave a better gelatin yield, and the extraction with pepsin gave a gelatin with higher molecular weight fractions (Cabeza et al 1999).

Enzymatic hydrolysis of chrome-tanned leather waste, have been studied that yielded hydrolysate of 50-60%. The same study indicated low ash content (2.4-3.3%) and low content of chromic compounds (13.6 - 54.5 mg per kg) for the dry weight of the hydrolysate (Langmaier 1999).

Collagen hydrolysate have been obtained by treatment of chrome shaving with enzyme. This hydrolysate has been used as a retanning agent and the performance has been studied (Cantera et al 2000).
Chrome collagen residues have been used to obtain gelatin using conventional methods. A large part of this type of residue has been used for the production of agglomerates known as regenerated leather, mixing with latex in dutch piles and various articles have been manufactured (Cot et al 2003).

Chrome shavings have been hydrolysed and the resultant hydrolysate/acrylic copolymer of the hydrolysate has been directly used as a retanning agent in post tanning process of leather making. The procedure helps for avoiding cost of disposal of shavings (Cantera 2003).

Two approaches for the utilisation of chrome shavings have been developed. In one approach an acidic protease-pepsin has been used followed by crosslinking with glutaraldehyde. The dried material has been used for leather board. The second approach is by using an alkali protease which completely digested the wet blue shavings into a smaller material. The dried material has been used for casein formulations in leather finishing (Crispim and Mota 2003).

A comparative study of alkali and enzymatic conditioning of “twinned” hide from calves, young and aged animals have been carried out. Some unique properties of gel strength and isoelectric point have been obtained. The results obtained from polyacrylamide gel electrophoresis and gel permeation chromatography of the gelatine yielded results showed that it has been possible to suggest a peptide-type collagen crosslinking developed with animal age (Cole and McGill 1988).

The hydrolysates of chrome tanned leather waste from tanning manufacture react with glutaraldehyde to produce thermo-reversible and thermo
irreversible gels. Thermo reversible gels have been employed as glues and thermo irreversible gels have been applicable in currently widespread encapsulation techniques (Langamaier et al 1999).

1.5 NEED FOR DEVELOPMENT OF PROTEIN BASED REACTIVE MATERIAL FOR LEATHER INDUSTRY

Many researchers and scientists have developed innovative methods for the treatment of solid waste to get useful product. Recoveries of proteins and greases have been explored (Comte et al 1974). Alkali hydrolysis has been used in many parts of the world for chrome recovery and for isolation of protein fraction (Btalle et al 1983). Acid hydrolysis has been used to convert the waste into a chromium containing hydrolysate usable in the retanning and fatliquoring steps of leather finishing (Taylor et al 1994). Extensive research has been carried out in the field of chrome shaving waste. The waste has been treated with alkali and enzymes to extract hydrolysed and gelable protein products and recyclable chromium cake (Taylor et al 2002). Further, the use of recovered chromium from shavings has been used as a retanning agent in chrome tanning process.

Gelatin preparation has also been carried out from chrome containing waste (Cabeza et al 1997; Cabeza et al 1998a). Keratin hydrolysate as a filling material for obtaining fullness and grain smoothness has also been studied (Ramamoorthy et al 1989).

Fleshing has been one of the major solid wastes generated in the leather industry. Fleshing alone constitutes 50-60% of the total wastes generated in leather industry. This creates a huge environmental problem if not utilised
properly. In this context, several researchers and scientists have explored the possible utilisation of fleshings for the conversion into useful end products.

Fleshings have been used as a raw material for the preparation of novel proteinoid for industrial application (Kanagaraj et al 2002) and proteinoid-acrylate composite having molecular weight in the range of 15000-20000 D for the application in leather processing operation (Kanagaraj et al 2001).

The major limitations associated with the products developed from fleshings have been bigger particle size leading to less reactivity to the collagen. Moreover, it does not contain any crosslinking group to stabilize the collagen in a better way. These limitations have prompted the researchers to look for better option to develop highly reactive material to stabilize the collagen in a better way. Since the fleshing contains mainly proteins, it can be hydrolysed to the level of amino acids these amino acids can be used to develop a highly reactive multifunctional polymeric substance which enables binding to the collagen as well as to tanning substances, thus increasing the reactivity as well as exhaustion of these tanning agents in the tanning process. An understanding of various studies in chrome tanning, vegetable tanning and other tanning systems is required for understanding the reactivity collagen to these tanning systems as well as exhaustion behaviour of these systems.

1.6 CHROME TANNING : POPULAR MINERAL TANNING

Chrome tanning is the one of the popular tanning systems followed worldwide. Basic chromium sulphate (BCS) at the level of 8-10% has been used for the tanning the pelt. Only a limited amount of 60-65% of the chromium is absorbed by the leather and remaining goes as waste causing huge pollution problem.
1.6.1 Various Parameters Employed in Chrome tanning

1.6.1.1 Mechanical action

It has been found that mechanical action plays an important role in transport of chromium ions into the fibre structure prior to tanning (Germann 1995). Mechanical action serves to flex the skin and create forces required to pump chrome liquor into the fibre structure primarily through pressure alterations within the connected pore structure of the matrix. The rate of penetration depends on the speed of agitation that in turn is influenced by the geometry and speed of the drum as well as cascadence ratios (De Simone 1986). The faster the rate of penetration of chromium, the higher the time available for chemical reactions between the metal ion and the protein sites.

1.6.1.2 Concentration of the solutions

Concentration of the BCS solution also play a major role in tanning process. The rate of the diffusion of BCS depends predominantly on the concentration; the higher the concentration in the float, the faster the chrome will penetrate into the fibre structure have been studied (Chandrasekaran et al 1989). Sulphate ion contained in BCS plays an important part in tanning (Gustavson 1956; Horman 1974). At high concentration of BCS, sulphate remains coordinated to chromium rendering Cr(III) species non cationic thereby (Gustavson 1956). Model studies conducted have shown that the rate of penetration is first order on Cr(III) or in other words rate of penetration is directly proportional to chrome concentration (Covington 1997).
1.6.1.3 Temperature

Several experiments have been carried in tanning out by employing temperature as one of the important parameter. The rate of diffusion of chromium species into the skin structure increases with temperature, when temperature is less than 50°C (Bickley et al. 1967).

An experiment consisting of low float with varying factors such as addition of alkali and temperature (50-60°C) had been carried out and compared with conventional chrome tannage. The chrome tannage carried out without the addition of alkali at the end of the tannage and without giving the usual aging period showed maximum shrinkage temperature of 50°C. The leather showed softer than that made by conventional method but slightly thinner and firmer. In another experiment when no alkali is added at the end of chrome tanning (less float) at elevated temperature but washing at 60°C, the results indicated increased chrome content and increased shrinkage temperature of the leather (Bickley et al. 1967).

1.6.1.4 Time

Reaction time between chromium and protein has been one of the important factor. It has been found that chromium fixation increases with longer process time, say up to a period of 24 hrs.

Chrome distribution in the leather of several tanneries have been carried out with various parameters such as time in chrome (3-5 h), temperature (33, 48°C), pH (3.2-4.5), percentage of chrome offer in leather (54-95%), spent tan liquor (1,3,44%). The author concluded that increase in tanning time
particularly during basification increases chrome exhaustion level (Covington 1981).

1.6.1.5 pH

The reaction between chromium and pH conditions have been studied by various researchers (Covington 1987). The reaction of chromium with collagen involves ionised side chain carboxyl groups of aspartic and glutamic acid residues with pKa values 3.9 and 4.3 respectively, at a temperature of 25°C (Stryer 1975). The rate of reaction depends on the number of ionised carboxyl groups on the collagen. It can be calculated that at pH 2, 3 and 4, the percentage of protein carboxyl groups remaining ionised is of the order of 1, 9 and 51% of the total respectively. In tanning practice, best results have been obtained by beginning at a lower pH and finishing at a pH around 3.8 - 4.0.

1.6.2 High Exhaustion Systems

It has been found that conventional chrome tanning method offers the uptake of chromium in the order of 40-70% of chrome used (Gauglhofer 1986). It has been now possible to increase the absorption levels of chromium in the tanning bath.

The closed-loop high exhaust tanning system based on alutan-chrome combination and ethanolamine assisted chrome tanning methods have been discussed. The technologies offer themselves as attractive zero waste options suitable to Indian leather industry. The methods provide shrinkage temperature of more than 100°C and exhaustion level of 90-95% (Chandrababu et al 1995). The high exhaustion technique showed chrome concentration of 19 mg Cr/l to
29 mg Cr/l for the upper manufacturing process (Luck et al 1987). The addition of calgon to basic chrome liquor reduced with saw dust increases the nonionic content of the liquor and decreases the fixation of chrome to collagen. The hydrothermal stability of leather made with calgon masked chrome liquor has been reduced. The leather produced by the latter type of tannage is soft and full and gave good nap in suede finish (Selvarangan 1982; Selvarangan et al 1983).

Chrome tanning carried out in a water-immiscible organic solvent led to a total exhaustion during the tanning process and chrome content in the aqueous effluents have been considerably reduced (Chagne et al 1993; Chagne et al 1996).

The reactivity of trivalent chromium salts towards collagen in organic solvent media with the effect of different factors, especially the nature of basifying agent on tanning have been studied in detail. The results showed that introduction of two bases phthalate and sodium bicarbonate into the medium giving a rise in pH of around 0.6 units per hour produced good quality leather and high binding of chromium to the skins. The presence of K⁺ ions attenuated binding of chromium salts to the skins. These ions lead to exchange of Na⁺ and K⁺ on the carboxylic sites of collagen at the expense of reaction with the chromium salts. Binding of chromium is better with paraphthalate than with orthophthalate (Silvestre et al 1993).

A novel tanning agent has been prepared from sulphonation of aromatic hydrocarbon (AHC) and complexing with commercial BCS salt using a polycarboxylic acid matrix at 80°C. A combination of tri and dicarboxylic acids has been introduced during complexation to prevent the metal ion from hydrolysis at high pH condition. The resulting mixture was neutralised to a pH
of 4.0 and used in leather processing. The results of the AHC showed chrome exhaustion at the level of 90-93\% and shrinkage temperature of 116-118°C (Thanikaivelan et al 2002).

Various options for reducing the chrome effluent in the tanning operation have been carried out. High exhaust chrome tanning (mechanical action, concentration, temperature, time, chrome offer pH). Tanning process modifications (marking, collagen reactivity, catalysis, chromium combinations) managing waste chrome streams (chrome liquor recycling, chrome recovery, chrome reuse) and chrome replacement (mineral tanning agents, have been discussed (Covington 1997).

1.6.3 Chrome recovery and reuse

The recovery and reuse strategy involves initially the separation of chromium from soluble neutral salts as chromic hydroxide (Covington et al 1983). Chromium (III) has been easily precipitated as chromic hydroxide by the addition of an alkali to spent chrome tanning solution (Hauck 1972; Covington et al 1983). Subsequently the precipitated chromic hydroxide has been redissolved by acidification. Technology packages for recovery/reuse method are readily available (Langerwerf 1999). Relatively low solubility of chromic hydroxide permits the easy and secure removal of chromium salts from spent tanning liquors. Supernatant liquors from chrome recovery plants have been relatively free of chromium and meet environmental standards for discharge viz. 0.3 ppm (Raghava Rao et al 1995; Raghava Rao et al 2002; Covington et al 1983).
Chromium uptake from regenerated chrome liquors from tanning has been comparable to the uptake from fresh batches of BCS. This method of recycling does not help to overcome the problem of dissolved neutral salts in the effluent. The reuse of supernatant solutions from chrome recovery plants in various pretanning operations is one of the inplant control approaches to contain TDS (Langerwerf 1999; Rutkowski et al 1998; Benrud 1951).

The waste stream contains nearly 30% of chromium and the waste chromium has been reused by either recycling the spent solution directly or after recovering the unused chromium as chromium hydroxide and regenerating as basic chromium sulphate for reuse (France 1975; Smith 1978; Davis and Scroggie 1980; Sharp 1981; Covington et al 1983; Langerwerf 1985; Raghava Rao et al 1999).

1.6.4 Use of External Aids in Tanning for High Exhaustion

Various exhaust aids have been used in chrome tanning to increase the exhaustion level of chromium. Tanning solutions contain Cr(III) species of relatively poor affinity to the protein matrix. Therefore, external aids to improve the exhaustion and uptake of chromium need to modify either the chemical species of Cr(III) or the reaction mode involved in the binding of the metal ion by the skin protein. It has been now possible to increase significantly the exhaustion levels of chromium through the use of external aids like keratin hydrolysate (Ramamoorthy et al 1989; Chandra Babu et al 1987; Kandeepan et al 1981; Suarez et al 1981; Selvarangan et al 1982; Jayaraman et al 1989). Chrome exhaust aids are based on a) polyamides, b) polycarboxylates, c) polyhydroxy aluminium chloride gels, d) long chain alkanolamines, e) polyelectrolytes. These exhaust aids may help in fixing more chromium by
creating additional sites for the interaction of chromium. Exhaustion levels of the order of 85-95% have been reached by making use of exhaust aids.

1.6.5 Modified chrome tanning salt

Chrome exhaustion level has also been increased by modifying BCS. This can be achieved by identifying the nature of molecular structure of major Cr(III) species not being absorbed during tanning and then evolving suitable methods to avoid the formation of low affinity species in the manufacture of BCS (Raghava Rao et al 1998).

1.6.6 Modifying the skin substrate for higher exhaustion

Increasing the number of metal binding sites in collagen can increase the reactivity of the protein in chrome tanning (Germann 1999). The simplest method to increase the number of carboxyl sites in collagen is to subject the amide side chain of asparagine and glutamine to alkali hydrolysis as in the case of liming. Another way of increasing the number of carboxyl group is to condense active hydrogen compounds containing carboxyl groups with the side chain amino groups of collagen using Mannich Reaction (Bowes and Elliot 1962; Ramasami and Ramaswamy 1975; Chandrasekaran 1987). Some significant improvements in metal binding capacity of collagen have also been reported by exploiting Michael reaction, where β-carboxy ethyl acrylate is covalently bonded to free amino side chains (Scholnick et al 1991; Scholnick et al 1992). Some molecular species of Cr(III) contained in BCS may be substitutionally inert (Ramasami 2001). Catalysing the reaction of inert species is potentially useful. It has been proposed that the improved exhaustion of chrome observed by the use of monoethanolamine during tanning may be
because of its ability to involve in hydrogen bonding with carboxyl groups (Covington 1997). The system based on monoethanolamine enables greater than 90% exhaustion of chromium (Prentiss and Prasad 1981; Chandrasekaran et al 1987; Covington 1998a).

Treatments capable of covalently binding aromatic 1,2-dicarboxylic acids to collagen have been described. The aromatic 1,2 dicarboxylic acid groups act as strong binding sites for chromium but not for titanium or zirconium. The shrinkage temperature of the modified collagen, after chrome tannage is exceptionally high (80-100°C), whereas the thermal stability after titanium or zirconium tannage is a little different from that attained by similar tannage of untreated collagen (Evans et al 1987).

The Michael reaction has been used with an acrylic acid derivative to provide additional carboxyl binding sites on collagen during processing of hides into leather. The crosslinked product had a higher shrinkage temperature and a considerably lower lysine and hydroxylysine content than conventionally processed hides. Subsequent tanning led to a higher chrome uptake than that found in the untreated control. The results indicated that both direct crosslinking and improved chrome tanning have been possible with this derivative but that these are accompanied by some loss of tensile strength (Scholnick et al 1991).

1.6.7 Direct recycling of spent solutions

The salt (NaCl 3.3 - 3.5%) present in the chrome streams has adverse effect on transport and uptake of the metal ion by skins (Raghava Rao et al 1999). For direct recycling of chrome in the chrome tanning stage to be technically viable, concentration of salt in the spent tanning solution need to be
reduced below 1% from a total of 7%. Hence, the reuse of spent chrome solutions in pickling rather than chrome tanning appears an attractive alternative. Reuse of spent tanning solution in pickling offer the advantage of containing salt pollution from tanneries (Davis and Scroggie 1973; Davis and Scroggie 1973a; France 1975).

To reduce the chrome pollutant, recycling of chrome tanning liquors have been described. The spent liquor has been recycled to pickle bath and tanning has been carried out. Six practical approaches of recycling techniques have been carried out, on average, one fifth of the normal chrome offer can be saved. It also gives the idea that instead of recycling spent chrome tan liquor into the main tannage, the retained liquor have been used in retanning blue splits. The economic benefit has also been more with more reduction of effluent load in tanning (Arnoldi and Covinton 1981; Sharp 1981).

Chrome recycling trials have been carried out and the resultant leather have been dyed and color properties have been compared. The chrome contents of the matching wet blue sides have been similar to the control sample. The leather produced by chrome recycling showed minimum variation in colour properties (Boast 1989).

Recycling trials have been carried out using commercial chrome powder. The chrome liquor has been reused for successive tanning runs after adjustment of the float and \(\text{Cr}_2\text{O}_3\) content to the desired values. The amount of sodium bicarbonate used for basification has been reduced in proportion to the amount of added chrome reagent. Recycling has been shown to be capable of saving more than 25% in the cost of chrome-tanning agent and to have the
added advantage of reducing the amount of chromium discharged in the tannery effluent to a minimum (Davis and Scroggie 1973b).

A method for the recycling of chrome tanning liquors has been proposed in which the spent liquor has been used as a basis for the preparation of pickle liquor. Two pickling systems have been tested in which either formate is omitted or is added before pickling with the pickle acid but in an amount reduced in proportion to the amount of added chrome reagent (Davis and Scroggie 1973).

A process for recycling spent chrome liquors from an organic acid pickle/tan have been described. This process enables the utilisation of almost complete chrome. Chemical costs are lower. The chrome tan effluent has been essentially reduced to zero. Salt is also eliminated from the tan procedure (France 1975).

Chrome recycling technique has been developed to decrease the amount of chromium discharged into the tannery effluent. The system is based on the pumping of the spent chromium solution from hide processors through a screening system and into a storage tank for equalisation. The equalised chrome liquor has been used as the pickle liquor (Pierce and Thorstensen 1976).

Various chrome tanning methods such as high exhaustion tanning, direct recycling of spent chrome liquors and chrome recovery and reuse and the effects on these methods on environment had been discussed. The naturally occurring chromium in soils and the uptake of chromium by plants, effects of chromium on waste water treatment plants soils, plants and animals are considered (Gauglhofer 1986).
By using microelectrophoresis, electrokinetic technique and the dye shift fixation as a function of pH the isoelectric point of chromium collagen has been found out. The results showed that cationic chrome tannage (i.e.) the regular type of chrome tanning, elevates the iso-electric point of collagen from pH 5-5 to pH 6.5-7.5 and the anionic chrome tannage shifts the isoelectric point of collagen to pH 4.0-4.5. The concept of chrome tanning postulating the stabilization of collagen by the formation of stable cross links between adjacent protein chains through the carboxyl groups entering into direct combination with the chromium atoms of the polynuclear complex is strengthened by this data. This data also provides the participation of hydroxy-amino acid residues (hydroxy-proline and serine) as coordination enters in secondary reactions appear more reasonable than the function of cationic protein groups as coordinators, from chemical and spatial considerations (Gustavson 1952).

Using differential scanning calorimetry, denaturation of collagen has been studied. The results indicated that denaturation occurs a narrow region centered at 68°C and a wide region at 85°C. It is concluded that there are two populations of collagen in the hide has been observed. But however, only the heat sensitivity of the less stable population is indicated by the shrinkage temperature as usually measured (Kronick and Buechler 1986).

The effect of three masking agents, sodium oxalate, sodium citrate and sodium orthophthalate on 33% basic chromium salt has been studied. The optimum concentrations of each of these masking agents, their synergistic effect and the corresponding shrinkage temperature and exhaustion of the tanning liquors have been studied. Oxalate in small doses of upto 0.2% may enhance chromium absorption and phthalate concentration of 1-1.25 results in improved exhaustion. The conclusion drawn is that phthalate is the best complexing agent
as for as masking basic chromium salts are concerned. The shrinkage temperature obtained is 95-96°C (Gregori et al 1993).

Investigations on self-basifying chrome tanning systems by using basifying agents like insoluble carbonates and masking salts like sulphate and formate, in addition to sodium bicarbonate, have been studied with respect to layerwise fixation and distribution of chrome, basicity and hydrothermal stability. In such a type of tannage there is not only uniform distribution of chrome but also higher fixation of chrome (Jayaraman et al 1972). It has been found that Chromic chloride solutions masked with salts of three organic acids (formic, acetic and oxalic) resulted in contain different size complexes in ion exchange of gel filtration with varying charges. It also showed that the distribution of the complexes varies with quantities of added salts (Takenouchi 1981). Masked chromium complexes have been studied for their charges in size and charge due to reactions with alkali. The size of the formato chromium complexes is not greatly changed by alkali but their charge is increased or decreased considerably according to the degree of masking. Aceto chromium complexes have been polymerised very strongly by alkali. The charge of the polymerised complexes depend upon the degree of masking. With the lower degree, their charge is cationic while with higher masking, the charge is anionic. Oxalato chromium complexes are little changed in both size and charge by alkali conditions. In some cases as alkali is increased the chromium complexes are readily precipitated (Takenouchi 1984).

An attempt has been made to develop a method for processing leather without pickling at the pH range of 5.0-8.0. It has been observed that chromium can penetrate to the pelt even during chrome tanning at higher pH values namely 8,7,6 and 5. The results showed that as the pH decreased from 8.0 to 2.8
the penetration of chromium increases, on the contrary exhaustion of chromium decreases. The exhaustion of chromium is amount 80% at the pH of 8.0 (Legesse et al. 2002).

The range and nature of reactions that contribute the stability of collagen with reference to hydrothermal stability have been reviewed. A new theory of the origin of hydrothermal stability with the relative contribution of entropic and enthalpic changes to collagen by interactive chemical process have been described. The reactions of various mineral tanning and organic tanning reactions have been explained by unifying model of collagen stabilisation (Covington 2001).

1.7 ORGANIC TANNING AGENTS AS ALTERNATIVES

Condensed or catechol tannin is made to react with some of the crosslinkers and the crosslinking effect has been studied. The preferred vegetable tannin is mimosa in which the presence of pyrogallol groups appears to aid the reaction. The preferred crosslinker is oxazolidine. Higher shrinkage temperature is achieved by (111°C) by heating to 60°C to drive the reaction. The pH requirements for fixing the two components of the tannage are mutually exclusive (Covington and Shi 1998).

The mechanism of vegetable tannins have been studied. It binds in two ways (1) to the backbone polypeptide groups of collagen by hydrogen bonding, and (2) to the basic amino acid groups, electrovalently for carboxylic acid containing tannins (Redlich 1966).
A comprehensive tanning study has been carried out with aliphatic dialdehydes. Glyoxal, was found to have the best tanning properties, ranking close to formaldehyde when employed at its optimum pH, which is between 9-10. The leather produced by this method showed a smooth-grained, strong and relatively soft leather. Apart from glyoxal, malonaldehyde and succinaldehyde can also tan the leather. Glutaraldehyde is shown to be a good tanning agent. Most of the aldehydes combine with amino groups of the collagen (Seligsberger et al 1957).

Pretanning with different aldehydes have been carried out. All the aldehydes included in this study underwent interaction with collagen and showed a tanning action as judged by shrinkage temperature and stabilisation of fibrous structure. The shrinkage temperature of the hide substance is increased by treatment at pH about 7.5-8.0 to approximately 75°C for succinaldehyde, 84°C for glutaraldehyde, 82°C for 3-methylglutaraldehyde, 78°C for 2,4 dimethyl 2 methoxymethyl glutaraldehyde, 76°C for α-hydroxydipaldehyde, 80°C for dialdehyde starch and 72-74°C for polymethoxy aldehydes. Formaldehyde and glyoxal increased the shrinkage temperature of collagen to approximately to 89°C respectively (Fein et al 1957).

Tanning by using different organic compounds such as polyaldehyde and secondary amines (diethylamine, dimethyl amine) have been employed and studied. Diethanol amine and isopropanol have been also tried. The results of the leather showed shrinkage temperature of 76°C-70°C with improved softness. This pretannage could reduce the consumption of chrome in the main tannage (Seigler 1987).
Tannin and protein interaction by electrovalent and hydrogen bonds and hydrophobic interaction have been studied. In addition, the fixation of tannin by various factors such as concentration of tannin, time and temperature, acidity and pH was studied (Bickley 1992).

Vegetable tanning penetrate to the collagen matrix by a hydrophobic interaction followed by secondary effect of hydrogen bonding has been found out. The oxazolidine undergoes ring opening, to form the N-methyolol intermediate typically postulated for other aldehydic tanning agent. In this case the next reaction is with the A ring of the polyphenol, causing a crosslinking of polymerisation thus favouring multiply bound tanning matrix is created within the collagen matrix (Bajza et al 1997).

1.8 SCOPE OF WORK

High reactive tanning system from proteinous source has emerged a simple and effective method for controlling problems of solid wastes.

A critical study of the present tanning practices and trends has indicated that improved exhaustion levels in both of two popular tanning systems – Chrome tanning and vegetable tanning have to be achieved for minimizing the effluent level.

Development of reactive tanning agents and their use in tanning will help in achieving exhaustion of tan liquors.
On the basis of the literature survey presented, there exists a scope for

i. the development of Reactive Protein (RP) from fleshing.

ii. use of this RP for tanning individually and optimizing the tanning conditions.

iii. use of RP in combination with chrome and vegetable tanning system.

iv. use of RP for high exhaustion in tanning processes.

v. use of RP in post tanning processes

The primary objective of the present study is to provide technological solutions to a) avoidable and minimisable problems of solid wastes particularly fleshing, b) help to overcome unavoidable problem of exhaustion level of chrome tanning and vegetable tanning through the development of high exhaust tanning system using RP.