

Solid wastes generation in the leather industry and its utilization for cleaner environment—A review

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Leather industry, one of the polluting industries because of generation of huge amount of liquid and solid wastes, also emits obnoxious smell because of degradation of proteinous material of skin and generation of gases such as NH₃, H₂S and CO₂. Solid wastes are raw trimmings, fleshings, chrome shavings, buffing dusts and keratin wastes. Accumulation of these wastes lead to sludge problem and choking of treatment pipes and finally results in reduction in efficiency of treatment plant. Treatment of solid wastes also is not cost effective, posing economic burden to the tanners. Leather industry in the developing countries is facing lot of solid wastes problem and many tanneries closed for not meeting bio-chemical oxygen (BOD) demand and total dissolved solids (TDS) norms. The objective of this paper is to review the kinds of solid wastes generated in leather industry and the useful technologies developed to overcome the solid wastes problem.

Keywords: Leather industry, Solid wastes, Useful end products

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Introduction

Leather industry has been categorized 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 m² of leather by 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 characterized 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 odor emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia and other volatile organic compounds are also associated with tanning activities.

Solid wastes generated in leather industries contribute mainly skin trimmings, Keratin wastes, fleshing wastes, chrome shaving wastes and buffing wastes. It constitutes protein as the main component. If these protein and other chemicals, which are present in the chemical treated protein, are not utilized properly it will pose hazardous pollution problem to the environment.

Raw Materials, Chemicals Used and Emission Factors in Leather Industry

Raw material for leather industry is raw hide or skin. 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^{1,2} used in tanning industry are lime, sodium sulphide, ammonium salts, sulphuric acid, chromium salts and vegetable tanning materials (Table 1, Fig. 1). Currently, about 6.5 million tons of wet salted hides and skins are processed worldwide annually. About 3.5 million tons of various chemicals are used for leather processing. A considerable part of this amount is discharged into the effluent. At an average consumption of 45-50 m³ of the waste liquor and 800 kg of solid wastes per ton of raw hide are discharged by the leather industry^{3,4}. The composition⁵ of liquid and solid wastes generated in tanneries worldwide are: COD, 1470; BOD, 619; suspended solids, 920; chromium, 30; sulphur, 60; and solid wastes (trimmings, fleshing, shaving & buffing dust), 3000 thousand tons.

Types of Pollution in Leather Industry Soil Pollution

Untreated wastewaters from tanneries have been applied on land merely to contain them at one place. The soils holding it directly and irrigated with contaminated groundwater lose productivity⁶.

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Table 1—Typical waste emission factors associated with leather processing

	Soaking	Liming	Deliming	Pickling	Chrome Tanning	Dyeing & Fatliquoring	Composite (incl. Washing)
BOD ₅	8.3-18.8	17.5-35.0	1.5-4.5	0.3-0.5	0.5-1.2	1.5-3.0	35.0-105.0
COD	22.5-45.0	35.0-87.5	3.8-10.5	0.8-2.3	1.5-3.8	3.8-10.5	87.5-280.0
Total Solids	262.5-415.5	105.0-175.0	6.0-15.0	26.3-52.6	45.0-90.0	6.0-15.0	528.0-875.0
Solids suspended	22.5-52.5	21.0-70.0	2.3-6.0	0.8-2.3	1.5-3.8	0.9-1.5	70.0-140.0
Solids chlorides as Cl ⁻	112.5-225.0	14.0-28.0	1.5-3.0	1.5-3.8	23.0-38.0	0.8-1.5	210.0-332.5
Chromium (total) as Cr	-	-	-	-	3.0 - 7.5	-	3.5-8.8

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

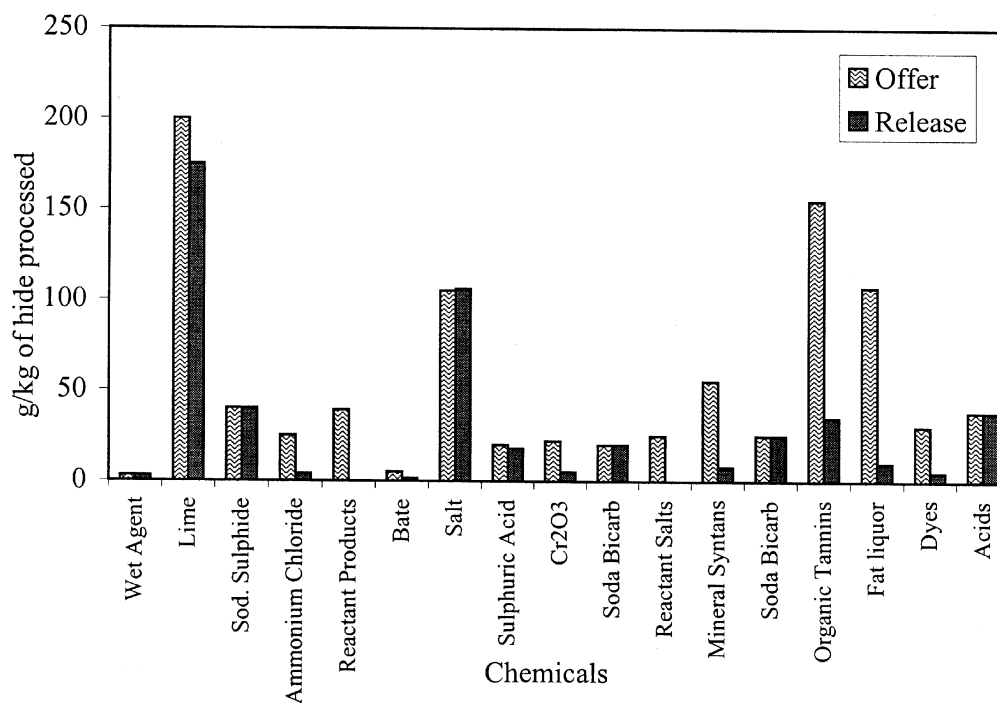


Fig. 1—Typical levels of utilization of chemicals employed in leather processing

Atmospheric Pollution

Tanneries are proverbially known for generating malodor. Rehydration of salted hides and skins generally emit odor of volatile fatty and amino acids evolved in the course of biological decomposition in presence of water. In addition, toxicity of hydrogen sulphide along with acids, fats, carbohydrates etc. in liming, deliming and tanning processes is predominant within 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/m³) in ambient air is lethal to human kind.

Ammonia escaping from deliming operation to atmosphere is odorous and pungent. Maximum admissible level of ammonia in air is 50 mg/m³. Phenolics (monohydric, dihydric and trihydric) are

emitted into air during processing of hides in the post-tanning and finishing operations. The permissible level of phenolics as phenol (C₆H₅OH) 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 reported⁶.

Waste Types in Leather Industry

Skin Collagen

Animal skin is composed of proteins (90-95 % of solids, 35% by wt), lipids, carbohydrates, mineral salts and water. Among several classes of proteins (collagen, elastin, keratin, glycoproteins, albumins and globulins), collagen is present in the largest amount and is responsible for the formation of leather by combination with tanning agents⁷.

Collagen fibres, enclosed in a connective tissue known as sarcolemma, are insoluble in water and in dilute solution of acids and alkalies and in organic solvents at ordinary temperatures⁸. Collagen possesses greater amount of swelling property in aqueous, acid and alkaline systems in absence of salt concentration. The important features of the collagen is three α chains with a repeating Gly-X-Y sequence staggered by one residue relative to one another⁹. Collagen is characterized by its high glycine content (33%), one glycine at every third residue. The ring structure of proline and hydroxyproline amino acids (22% of total amino acids) prevents rotation about the N-C α bond in a polypeptide chain. In addition, model studies and energy calculation show that rotation about C α -C=O bond is 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 and 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 suggested¹⁰.

Solid Wastes

Out of 1000 kg of raw hide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather. Tannery generates huge amount of solid waste as follows: fleshing, 50-60; chrome shaving, chrome splits and buffing dust, 35-40; skin trimmings, 5-7; and hair, 2-5%. Solid wastes in the leather processing constitute: beam house, 80; tanning, 19; finishing, 1%. The solid wastes can be hydrolyzed and used as a useful byproduct¹¹ in many ways (Fig. 2).

Solid Wastes Generation and Utilization

Keratin Wastes

Keratin is difficult to hydrolyze and highly resistant towards enzymes and most of the chemicals. It is rich in cystine. Keratin has been hydrolyzed using conc. NaOH or HCl. 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 altered¹².

Fleshing Wastes

Fleshing (50-60% of the total wastes generated in leather industry) has been explored for the possible utilization into useful end products¹³. Modified fleshing hydrolysate, prepared from fleshing and acrylic acid¹⁴, 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^{15,16}.

Limed fleshings have been utilized for stabilizing the delimed pelt, which has been named as Reactive Protein (RP). It has been developed from specific chemical treatment by oxidation and reduction method to convert some of the amino acids to aldehyde, which can be used as a tanning agent for stabilizing the pelt. RP has been treated to the delimed pelt and tanned. Tanning studies with chromium and vegetable tannin showed that RP could give improved leather properties. The system was optimized and mechanism was studied¹⁷. Fleshings, the major solid waste generated at the pretanning operations of leather processing, were hydrolyzed using pancreatic enzymes. Proteolytic activity of pancreatic homogenate showed a 6-fold increase in proteolysis against the control at the end of 7 days. Total protein content, collagen and free fatty acids in the hydrolysate supernatant were 80.0, 10.64 and 72.86 mg/ml respectively. The optimum pH for the enzyme preparation was 8.5. The hydrolysis was observed by almost total liquefaction and the fleshing was dried. The hydrolysate, as a protein source, could be used as a feed formulation by mixing with other feed ingredients¹⁸.

Chrome Shaving Wastes

Chrome tanned leather, splits and trimmings have been useful in obtaining glue, gelatin, protein flavor 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 (95%)^{19,20}. Chrome shaving hydrolysed using magnesium oxide alone or in combination with calcium hydroxide, sodium hydroxide or sodium carbonate increase efficiency of the solubilization and at the same time reduce the amount of enzyme needed

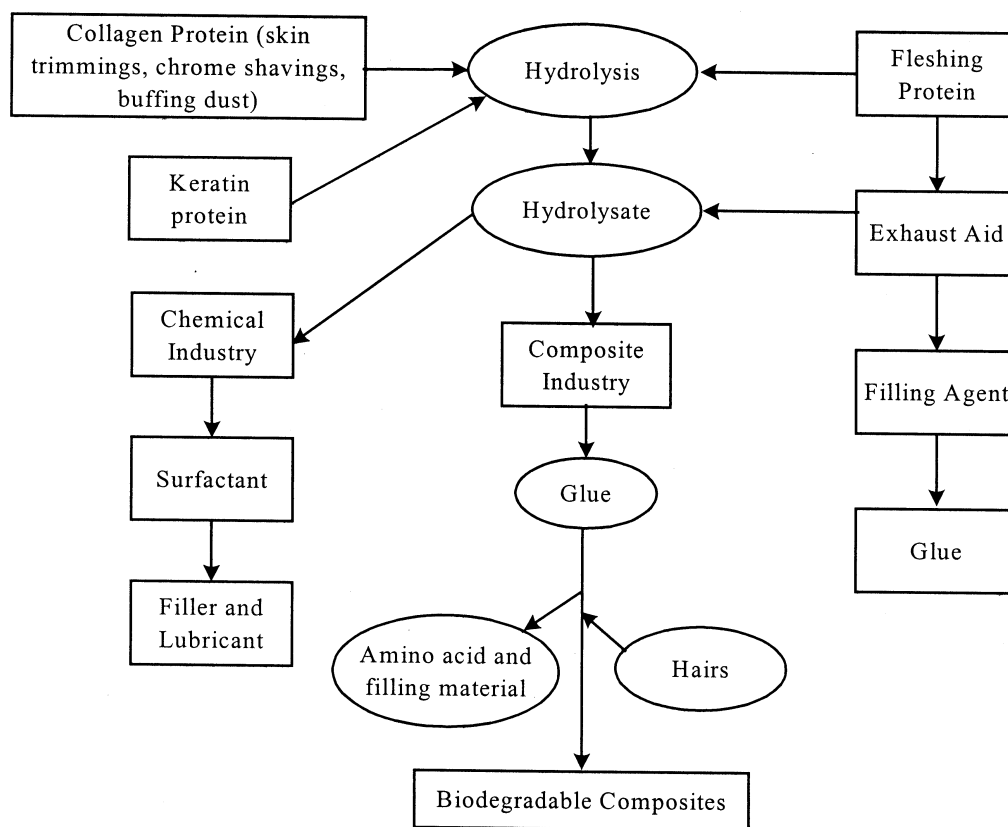


Fig. 2—Flow diagram of solid wastes utilization

and thus making the treatment more cost effective²¹. It has been found that there is no migration of Cr(III) at actual land disposal sites²². 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 way²³. 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 sites²⁴.

Gels, adhesives and films of high molecular weight gelable protein fraction have been obtained from chrome shavings under mild alkaline conditions. However, characteristics of the products depend on composition of the original chromium waste product and on the specific treatment conditions^{25,26}. Wet air oxidation peroxide treatments and incinerators at a variety of temperatures have been used for the recovery of chromium²⁷⁻³⁰. Several researchers have detanned the chrome product for gelatin preparation and isolation of collagen fibres^{31,32}. Chromium containing leather waste can be treated with enzymes, but only after pretreatment to denature the collagen^{33,34}.

Methods developed at this laboratory demonstrated that collagen may be denatured in the presence of alkali at moderate temperature, such that enzyme may be added directly to the alkali treated shavings. Maintenance of these temperatures at the enzyme digestion process eliminates the need for additional cooling equipment^{35,36}.

The gelable protein products isolated from treatment of chromium containing leather waste have high ash content not only because of the alkali and to extract the gelable protein, but also because of high mineral content in the original substrate³⁷. During commercial preparation of gelatin, it is common practice to pass the protein solutions through ion-exchange resin in order to lower the ash content and improve quality of the product.

Chrome shavings have been treated with proteolytic enzyme at 60-65°C in the presence of lime (5-6%). From this, protein has been separated by filtration leaving chromium cake. The protein hydrolysate (< 4.5 ppm chromium) is potential as a feed, fertilizer, or as an additive in the cosmetic industry³⁸. The interaction of gelatin and polyphenols has been studied³⁹. Galloyl

and polyphenols possess hydrophobic sites. 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 using magnesium oxide (MgO), carbonates and hydroxides. Carbonates and hydroxides have a detrimental effect whereas MgO has the most significant effect^{40,41}. 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^{42,43}. Chrome shavings have been used for making chrome cakes. The unwashed chrome cakes showed: moisture, 83.9; ash, 40.57; Total Kjeldahl Nitrogen (TKN), 6.07; and chromium (Cr₂O₃), 4.2%^{44,46}.

Partially hydrolysed collagen is one of the useful end products developed from chrome shavings. Modification of the process at any of the several points may alter the characteristics of the protein product and thus improve its market potential. Partially hydrolyzed collagen fractions extracted from chrome shavings treated with MgO (<6%) alone or in combination with sodium or potassium hydroxide (0.25-2%) or sodium or potassium carbonate (1 or 2%) were evaluated in terms of molecular weight determinations and thermal stability. All the samples were from the gelable protein category. SDS-PAGE showed that, in most cases, protein (60%) fragments were equally divided between intermediate (50-100 kDa) and large sized fragments or peptide (< 50 kDa) fraction and the remainder in the >200 kDa fraction. The fraction when kept in solution at 5°C for at least 15 h, these protein fractions developed the triple helical (30-60%), which confirms of a comparable concentration of native collagen. Melting point (T_m), for the helix to coil transitions were 22 +2°C for all samples studied.

Chrome shavings have been pretreated at 67-69°C with anionic surfactant in water (500% float) for 2 h. Pretreatment with MgO to maintain the pH, alcalase (Novo Nordisk) 345 ml has been added and left for 3 h. After the enzyme digestion, high quality of

gelable and protein products have been obtained from chromium containing leather waste. 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. Protein hydrolysate from chrome shavings markedly increases biodegradation of material and also exerts a positive influence on mechanical properties⁴⁷.

Chrome shaving wastes can be hydrolysed by enzyme⁴⁸ using alkaline proteases *Alcalase* (0.03%). Under mild reaction conditions, a soluble collagen hydrolysate is formed and a solid fraction (so called chrome cake) with high chromium content is formed after filtration. Further use of the chrome cake e.g tanning bath recycling, necessitates a maximum possible reduction in the protein fraction. Decantation washing of the chrome cake obtained after two-stage enzymatic hydrolysis of chrome-tanned shavings was performed 6 times with drinking water at laboratory temperature. Chrome cake was further deproteinated by means of addition of enzymes *Esterase* (0.05%) and trypsin (0.05%). The results showed that the enzyme split the protein chains between amino acids glutamine-histidine, serine-histidine, leucine-valine, leucine-tyrosine, tyrosine-threonine. Trypsin attacked protein molecule only in peptide bonds, where one of the amino acids is arginine or lysine⁴⁸.

Chrome shavings have been treated with pepsin A (3900 units/mg) and trypsin (10, 400 units/mg) for 6-24 h at the optimum pH of 8 and gelatin was 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 yield⁴⁹. Chrome shavings treated with pepsin-trypsin and pepsin-alkaline proteases have yielded products such as gelatin, chrome cake and hydrolysate^{50,51}. Chrome shavings (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 process⁵¹. 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 leather⁵²⁻⁵⁴.

An acidic protease-pepsin has been used followed by crosslinking with glutaraldehyde. The dried

material has been used for leather board. An alkali protease completely digested the wet blue shavings into a smaller material. The dried material has been used for casein formulations in leather finishing⁵⁵. 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 gelatin showed that it was possible to suggest a peptide-type collagen crosslinking developed with animal age⁵⁶. Hydrolysates of chrome tanned leather waste from tanning manufacture react with glutaraldehyde to produce thermo-reversible and thermo irreversible gels; former have been employed as glues and later in currently widespread encapsulation techniques⁵⁷.

Chemical or biological degradation of chrome shavings results in collagen hydrolysate and chrome cake. To add value to the recovered collagen hydrolysate, immobilisation of degradative enzymes using organo phosphorous hydrolsae (OPH) has been shown to be effective in degrading a range of organophosphate esters. A crude extract of OPH from Flavo bacterium sp was immobilized onto collagen hydrolysate films. The resulting film showed continuous and recyclable activity for degradation of a model organophosphorous compound, paraxon⁵⁸.

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 duct piles and various articles have been manufactured^{59,60}.

Conclusions

Solid wastes generated in the leather industry pose pollution problem in terms of sludge, BOD and TDS. Raw trimmings and wet blue trimmings are useful in developing glue and gelatin. Keratin hydrolysate can be used as an exhaustive aid for chrome tanning. Similarly fleshing hydrolysate can also be used as a tanning agent by proper chemical modification. Fleshing wastes can also be used to develop glue, gelatin and poultry feed. Chrome and buffing dust are useful in developing retanning agent, poultry feed, fertilizer and landfill sites.

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