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Leather Processing Technologies: A Review

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ABSTRACT

Tanning industry is one of the oldest industries in India. It involves conversion of animal hide or skin into an end product useful for making leather goods. There are several processes involved in leather making, one of the process is tanning. Tanning of the hide is done either by vegetable tanning or by chrome tanning process. In most developing countries tanning operations is a family business, carried out in small to medium scale semi-mechanized units, very frequently grouped tightly in clusters which used to be outside residential areas. The disposal of these chromium effluent into water bodies is known to cause various ill effects. To replace that, vegetable tanning can be practiced, where the method is easy as well as eco-friendly.

Keywords: Tanning, chromium, vegetable, tannins, eco-friendly.

Introduction

The global leather industry generated about 18 billion square feet leather in 2003 with an estimated price of US$40 billion. Most developing countries including India is producing 60 % of world's leather needs. For making the leather, Tanning is considered as a major process which involves more chemical reactions as well as mechanical operations. During the process more chemicals including chromium, acid solvents etc. are involved, these processes release effluent of 30L/kg of processed skin, where tanneries of India are releasing effluent more than 50,000 mg/day with huge quantity of organic pollutants. 70% of chrome (III) is usually discharged and leads to heavy metal contamination in water. Release of chromium by tanneries are higher now than mentioned parameters. Chromium, a major heavy metal exploited in leather industry. In India, it was found to release 30 billion of waste water with 3000-5000mg/L of total solids and chromium in between 100-200mg/L on processing 700,000 tons of skins in about 3000 tanneries. More than 170,000 tons of with 0.04Mt Cr (III) wastes per year are released into environment worldwide. With the enhancement of environment realization and change in manufacture patterns, the world industry is desirous to take cleaner and greener approaches for leather processing. The global leather has been in existence during which technologists were concerned to inflict stability to raw skins and hides. Until the approach of chrome tanning, there were very few options available for tanners such as aluminium tawing, smoke tanning, oil tanning and vegetable tanning. The term tannin was firstly used in 1796 by Seguin in order to specify the specific components of

vegetable extracts having a potential to bind with collagen making insoluble complexes by blocking the action of other proteolytic enzymes which effect the physical condition of the skin Chakraborti et al. (1966). The process of this extraction may include non-tannins and other materials which have no tanning strength which contributes in determining the functional properties of the leather. Oils of animals Leather are also smoke tanning where the oil in animal's brain used as tanning agent which gives highly durable leather. Today chrome tanning is the most commonly used method which accounts for world's leather production. Although chrome tanning has many advantages like high speed, low cost, good hide storage, etc. 40% of the chromium remains in the effluent which end up in sludge. One of the major problem of leather industry is chromium disposal where the treatment results in chromium contaminated sludge. Due to these disadvantages of chrome tanning tanners are encouraged to use the eco-friendly process of tanning like vegetable tanning.
The tanning industry is known to be very polluting especially through effluents high in organic and inorganic dissolved and suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues. Disagreeable odour emanating from the decomposition of protein solid waste, presence of hydrogen sulphide, ammonia and volatile organic compounds are normally associated with tanning activities. A significant part of the chemical used in the leather processing is not actually absorbed in the process but is discharged into the environment. Liquid effluent from leather processing contains organic matter, chromium, sulphide, and solid waste includes fleshing, wet blue splits, trimmings and shavings, buffing dust etc. Tanners in such units have no formal education and have little or no understanding of the complexities of the leather processing, their skills acquired from their elders with hardly any perception of environmental protection low waste technologies, generally speaking, require better skilled personnel and closer technical control than conventional processing Ravindranath et al (2000).

The study was aimed to assess the technology used in leather production and waste disposal, in tanneries. Leather units which use many toxic chemicals, are the single largest contributor to the pollution of the surface as well as groundwater. This location was optimal in the early days, because the tanning activity was kept outside of the city area (so that stench and waste would not be a problem for the city dwellers). Also, to have access to water was important because the tanning industry has a high consumption of water.

History of tanning

Tanning is one of the ancient trades of humanity in reference to use of leathers in archaeological sites and cave paintings. Tanning had a random nature which has evolved slowly into craft in the middle age. The scientific studies on tanning started in nineteenth century and derived into present day leather technology with the development of machinery and industrial revolution. The Egyptians made long-lasting leather which is 3000 years' old specimen but still in good condition which made the evidence for oil tanning. At first the skins obtained from hunting and livestock breeding were used for clothing and tents but they became stiff at low temperatures and rotted with heat which was overcome after many attempts by a process called smoking where the animal fats were rubbed for getting more render and flexible and this process became an origin for leather processing by accident. From middle ages till 17th century there was no change in skin processing. At the end of18th century with the development of industrialisation created a demand for different types of leathers for belting in machines, leathers for textiles, footwear, fabrics, etc. Similarly, at the end of 19th century the tanning industry was developed with the discovery of various chemicals as tanning agents and finally with the discovery of major tanning agents like chromium and alum pointed the beginning of industrial scale tanning. According to references, it is Neolithic period where man started using plant materials such as bark, pods, leaves to prevent skins from putrefaction forming the most stable and durable material. The term skin is the one used to determine the outer part of mature animals of smaller type such as Pigs, goats, reptiles, fish, etc. whereas the term hide is referred as the outer part of large animals such as buffalo and cattle Raji et al (2019).

The objective of the study was:

1. To study the technology adopted by tanneries in production of leather from hides and disposal of solid and liquid waste.
2. To identify the environmental friendly technologies related to leather industry.

Steps involved in leather processing

1. Soaking
Soaking is the first step involved in tanning where the preserved raw skins or salted skins are treated with water to make the skin dirt free and soft. The main purpose of soaking is to remove salt, rehydrate the dry skin and also to remove unwanted materials like blood, soil, dung, etc. The soaking time depends on condition of skins or hides.

2. Liming
The second operation is liming which involves the removal of hair and unwanted materials which are not transferred to leather. It also loosens the epidermis and also remove soluble skin proteins. It uses lime and sodium sulphide as liquor. The hair is loosened due to increase in high pH. The higher pH also causes splitting and swelling of fibre bundle. Dehairing and fleshing is also done in order to remove extra flesh and allow tannins to penetrate easily.

3. Deliming
Deliming is the process of adjusting pH between 8-9 which enhances the enzyme activity and onverts proteins into soluble forms. It uses ammonium sulphate and results in de-swelling of pelts. Deliming decreases the plumping of skin or hide.

4. Bating
Bating makes the grain surface soft and flexible. It prepares skin for tanning. It is anenzymatic operation which removes unwanted proteins and increases the degree of stretch. It imparts flexibility and softness towards the leather.

5. Degreasing
Degreasing is a process used to remove extra fat and oils which allows the tannin to penetrate easily through the skin. This step can be carried out by emulsion of fats using detergents or surfactants.

6. Tanning
Tanning is the main operation which converts skin or hide to stable material called leather. In this step tannin is allowed to interact with the prepared skin which act on collagen and make it stable.

7.Fixing

Formic acid is mostly used in this process which ensures homogenous tanning of hides in leather processing. Tanning is a process that stabilizes the protein of the raw hide or skin so it does not putrefy, making it suitable for a wide variety of applications. The various steps involved in tannery industry is given in Fig-1 volume of effluent generated during various process is given in table 1. Characteristics of combined effluent of beam house and tan yard is given in table 2, specific tolerance limit for effluent of chrome tanning and veg tanning is given in table 3.

Types of tanning

A. Mineral tanning
Mineral tanning is a process which uses basic chromium sulphate as tanning agent after the process of pickling. Once the desired level of penetration the pH is again increased to facilitate the process which is termed as basification and the obtained product is called as wet blue.

B.Tawing
Tawing is another practice which uses aluminum salts and alum along with other materials such as flour, egg yolk and other salts. It is an age old traditional process which gives a wet white product. In this method the skin is tawed in alum and salt solution which increases flexibility, stretch ability, etc. whereas egg yolk and flour enhances the handling properties. Tawing was conventionally used on goat skins and pig skins.

C.Chrome tanning

Chrome tanning is the most commonly used tanning process. It uses Chromium (III) sulfate which has been considered as the most effective and efficient tanning agent. It forms polychromium compounds by a process called olation which acts as active compounds in tanning that crosslinks the collagen subunits. The leather obtained by chromium contain 4-5 % of chromium and its efficiency is determined by enhanced hydrothermal stability and resistance to shrinkage at high temperature. Although chrome is an effective tanning agent it is having some hazards towards human Tare et al (2003).

Effects of chrome tanning on human

Chromium in its +6 oxidation state is referred to as Hexavalent chromium. It is mainly used for coatings, wood preservation, dyeing, etc. The chromate mimics the sulphate in its structure and surface charge which can enter the cell and cause cancer, eye irritation and skin allergies. There is a high risk of getting cancers to the workers exposed to hexavalent chromium for a prolonged time. It has been reported lung cancer among workers in chromium chemical production. Repeated exposure to hexavalent can also damage the respiratory tract and may also cause nasal cancer. Direct eye contact of chromate causes permanent eye damage and eye irritation. Prolonged exposure to skin cause skin allergies, dryness fissured skin, skin ulcers and swelling. In other way some workers may develop allergic sensitization where exposure to small amount cause serious skin rash. Other effects of chromium include dizziness, growth problems, reproductive disorders, discoloration and erosion of teeth.

Vegetable tanning

Vegetable tanning is the most suitable eco -friendly process which results in release of less pollutants to the environment. Vegetable tanning involves usage of tannins extracted from various parts of a plant. It mainly depends on amount of tannins in the extract which can be determined by various methods such as Folins Denis method, Mass spectrophotometer, UV detection, Reverse-phase High pressure liquid chromatography (HPLC), Mass spectrophotometer, nuclear magnetic resonance and Circular dichroism. Vegetable tanning is a two stage tanning which includes fixing and penetration. Penetration involves diffusion of tannins into the skin whereas fixing makes the penetrated tannins bind with collagen forming stable material. It is mainly affected by several factors such as temperature, pH, mechanical actions and particle size. The pH is the most important factor that affects the penetration and fixing of tannins. The reduction of pH in tanning liquor increases the potential of collagen fibres to swell and increasing the tendency of tannins to bind with collagen. Temperature is another most important parameter which affects the vegetable tanning. Increase in temperature results in high diffusion of tannins and gives high degree of tannage. Acid and salt content in tannin liquor greatly influences the physical condition of leather. Control of these parameters results in production of most stable and flexible leather which results in release of less contaminants and thereby protecting the environment. Hence the current study is an eco-friendly approach which reduces the toxic waste generation when compared to chrome tanning process and thereby reducing environmental impacts by contributing towards greener or cleaner development of leather processing Shivacoumar et al.(2000).

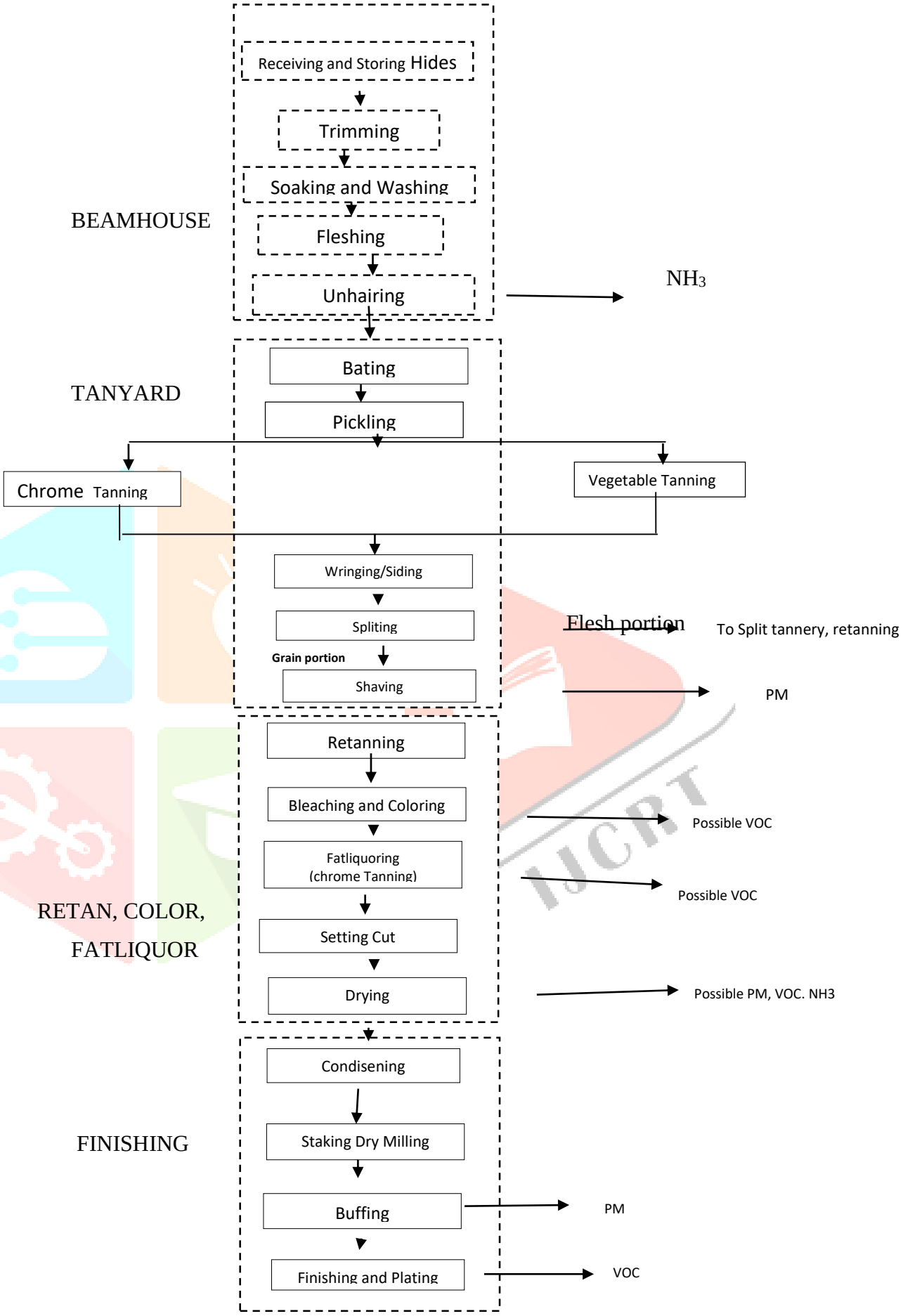

Figure -1. General flow diagram for leather tanning and finishing process.

Table-1. Volume of effluent treatment generated during various processes of tanning

S.NO.	Process	Volume of liters per 100 kg. hide of skin processed
1.	Soaking	250-400
2.	Liming	650-1000
3.	Deliming	700-800
4.	Vegetable tanning	200-400
5.	Pickling	200-300
6.	Chrome tanning	400-500
7.	Composting (including washings)	3000-3500

Table-2. Characteristic of a vegetable tanning effluent (combined effluent of beam house and tan yard)

S.no.	Characteristic	Result
1.	Color	Brownish
2.	Odor	Disagreeable Foul odor
3.	pH value	8.5
4.	Total Solid, mg/l(105^0C)	17640
5.	Total Suspended Solid mg/l	5990
6.	Total Dissolved Solid mg/l	11650
7.	Dissolved Fixed Solid mg/l	10520
8.	BOD (5Days at 20^0C) mg/l	1200
9.	Permanganate Value (4hrs) mg/l	320
10.	Chlorides (as Cl), mg/l	6700
11.	Sulfides (as S) mg/l	22
12.	Sulfates(as SO_4) mg/l	360
13.	Ammoniacal Nitrogen (as N) mg/l	21.3
14.	Total Kjeldahl Nitrogen (as N) mg/l	78.9
15.	Calcium + Magnesium (as $CaCO_3$), mg/l	1490
16.	Percent Sodium (as Na),	84.7
17.	Oil & Grease, mg/l (petroleum ether solvent)	16
18.	Tanning & Lining compounds (as tannic acid), mg/l	50

Table-3. Specific tolerances for effluents of chrome tanning industry

S.no.	Characteristic	Tolerance limit
1.	Chlorides(as Cl) mg/l	1000
2.	BOD (5 Days at 20^0 C), mg/l	30
3.	Hexavalent Chromium(as Cr)mg/l	0.1
4.	pH value	5.5 to 9.0
5.	Color & Odor	Absent

Chemicals used in tanning

Tanning is especially polluting in countries where environmental regulations are lax, such as in India, the world's third-largest producer and exporter of leather. To give an example of an efficient pollution prevention system, chromium loads per produced ton are generally abated from 8 kg to 1.5 kg. VOC emissions are typically reduced from 30 kg/t to 2 kg/t in a properly managed facility. A review of the total pollution load decrease achievable according to the United Nations Industrial Development Organization posts precise data on the abatement achievable through industrially proven low-waste advanced methods, while noting, "even though the chrome pollution load can be decreased by 94% on introducing advanced technologies, the minimum residual load 0.15 kg/t raw hide can still cause difficulties when using landfills and composting sludge from wastewater treatment on account of the regulations currently in force in some countries Majoomdar et al (1998). The tanneries effluent disposal unit was dumping 22 tons of chromium-laden solid waste per day in the open.

Enzymes like proteases, lipases, and amylases have an important role in the soaking, dehairing, degreasing, and bating operations of leather manufacturing. Proteases are the most commonly used enzymes in leather production. The enzyme must not damage or dissolve collagen or keratin, but should hydrolyze casein, elastin, albumin, globulin-like proteins, and nonstructural proteins that are not essential for leather making. This process is called bating. Lipases are used in the degreasing operation to hydrolyze fat particles embedded in the skin. Amylases are used to soften skin, to bring out the grain, and to impart strength and flexibility to the skin. These enzymes are rarely used. Exposure to long periods of low relative humidity (below 40%) can cause leather to become desiccated, irreversibly changing the fibrous structure of the leather. Chemical damage can also occur from exposure to environmental factors, including ultraviolet light, ozone, acid from sulfurous and nitrous pollutants in the air, or through a chemical action following any treatment with tallow or oil compounds. Both oxidation and chemical damage occur faster at higher temperatures. Various treatments are available such as conditioners. Saddle soap is used for cleaning, conditioning, and softening leather. Leather shoes are widely conditioned with shoe polish. Morena et. al. (2011).

Waste Water Treatment Plant

The main component of contamination is organic loading which is represented in terms of Biochemical Oxygen Demand (BOD) and inorganic load as Total Dissolved Solids (TDS). the efficiency of the plant generally found around 65%. This is due to lack of funds available for operational and management costs. The wastewater is highly corrosive and damage iron bolts and pipes. It is the responsibility of tanners to remove chromium from their effluent. The tanners producing more than 50 leather hides per day, big tanners, are installed with chrome removing facility but they do not abide by the law and do not care for the environmental degradation Thanikaivelan (2004). It is favorable to remove chrome at the source because it is easier and beneficial from the tanner's point of view since he can convert the hexavalent chrome to trivalent chrome and recover it to save his cost on raw material. But their ignorance has not only elevated problems for them but also created problems for the environment. India's leather industry occupies a prominent role in international trade, generating foreign exchange and providing employment. The industry employs more than 2.5 million people. Much of the economic benefits derived from leather production and trade, however, have typically come at considerable cost to the environment and human health. The study has presented important findings and analyses, leading to an enhanced understanding and appreciation of the multiplicity of barriers and

opportunities for the further development of the Indian leather sector. It shows how democratic structure shatters when every individual defends his failures with other's shortcomings. As for the common man, this ignorance has led to financial, social and health related problems and they feel desolated on their own land. The Common Effluent Treatment Plant (CETP) is not equipped to deal with chromium. The plant works under capacity due to insufficient financial support. This result in increase in concentrations of chemical constituents beyond their standard levels lay down by government. The chromium released by the tanneries goes untreated to join river or agricultural land for irrigation. The most important explanations of firms" non-compliance with environmental regulations are that the enforcement of the regulations is poor and fraudulent, that many of the tanners believe their activity does no harm to the environment, that there is no customer or market demand for cleaner production. Chromium enters in food chain. These irregularities have had a disastrous economic, social and health impacts. Most of the developing countries are facing acute shortage of technically qualified personnel for the operation, monitoring and maintenance of effluent treatment plants for tannery wastes. Appropriate training and education programmes are needed to cater for the needs of technical personnel at various levels (operating, supervisory, managerial and design). There is an urgent need to prepare a working paper which precisely identifies a training curriculum, type of faculty and infrastructural facilities required for this purpose Tare et. al.(2003) The existing expertise and facilities available in some of the developing countries should be taken into consideration for the regional needs. It is believed that by combining strict process control, good housekeeping measures and cleanliness, introduction of recycling of some floats, predominantly aqueous finishing together with simple treatment of wastes it would be possible to eliminate nearly 50 percent of the total pollution load discharged into the environment with only marginal investment.

Leather and environment

Processing industries are causing much damage to the environment. Leather processing is one such industry which takes skins from meat industry and processed to produce leather through tanning process. It gained negative impact in society because of its pollution. Leather processing involves various operations which include many chemicals that are expelled out in processing. 40 litres of water is required for processing 1kg of skin which results in generation of large amount of effluent leading to increase in Biological oxygen demand and Chemical oxygen demand. It also results in emission of chromium and sulfate ions. Leather industry also emits obnoxious smell due to protein degradation of the skin and results in generation of toxic gases such as ammonia, H_2S, etc. According to the research data only 20% of the raw hide is used for production of leather where the remaining is generated as waste. Hence leather industry is considered as one of the major polluting industries which generates huge amount of solid and liquid wastes Govindan (1985). The most important approach for prevention of environmental pollution is getting an idea prevention is better than reuse which is better than disposal of wastes. There are various recycling methods to make generated leather wastes into eco-friendly useful bi-products such as production of fat liquoring oils and bio-diesel from pre-fleshing wastes production of activated carbon, gelatin, retanning agents etc., from shavings and trimmings, production of grease, methane gas, fertilizers, etc., from fleshing waste. Hence cleaner production and recycling are the best options in order to control environmental pollution.

Remedial measures

Several remedial measures are suggested to lessen the environmental impact of tanneries. In large and medium sized tanneries environmental management system must be developed. Staff should be trained for occupational health and safety. Gaseous masks must be provided for workers in order to prevent inhalation of fumes. Proper arrangement must be made to stop use of tanneries solid waste to make poultry feed. Improvement in drainage system is needed to avoid the formation of hydrogen Sulphide in the tannery. Many options are available for reuse of chrome, discharged in the tanning effluent. This includes direct recycling of chrome tanning float, recycling of chrome after precipitation, and use of tanning products that improve the exhaustion rate. One feasibility study shows that in conventional chrome tanning process 25-30% chromium goes into wastewater. The recovery cost of this is only 30% of the chromium recovered, hence the entire system has a payback period of less than a year. Wastewater should be treated at two levels: primary and secondary. Primary treatment is consisting of mechanical screening, pH levelling, coagulation and flocculation, and sedimentation. Secondary treatment uses biological processes to remove most of the organic matter form the wastewater Sujatha et. al. (1995). For secondary treatment of wastewater of tanneries many treatment technologies are available like activated sludge, percolating filter, aerated lagoon, facultative lagoon etc. however, considering the organic and hydraulic load of the tanneries it is inferred that activated sludge

treatment is best suited for secondary treatment. In activated sludge treatment the wastewater is introduced in a tank aerated by mechanical stirring or by compressed air. After sufficient contact time the mixture is clarified in settling pond and sludge is recycled in the aeration tank. The excess sludge from the system is treated with the primary sludge. This is a proven technology for the treatment of tannery wasted world-wide.

Conclusion:

Even though the Indian environmental regulations for the tanning industry are equally stringent as the international regulations, the pollution load coming from the tanneries is still heavy, and it is a problem both for the people living nearby, and for the river and ground water. There is a wide gap between the environmental regulations for the tanning industry and the environmental performance among the tanneries in the Kanpur area. Though few tanneries have the prescribed equipment to do primary treatment but most still fail to operate them properly or at all. Many of the tanners. believe their activity is not harmful to the environment, or they do not see the environment as something that needs to be protected or treated properly. Thus, lack of properly trained staff at different levels remains one of the crucial constraints.

Recommendations

The above study shows the harmful effect of numerous chemicals generated by the leather industry. Chemical recovery and reuse is an economically feasible alternative for the leather sector. With their short payback period chemical recovery plants are financially attractive options. Leather industry should make all attempts to reduce its impact on environment by making every effort to reuse and recycle chemical compounds. Following steps may help in making the leather industry environmental friendly.

1. Training programs on occupational health and safety and modern practices of handling chemicals should be conducted.
2. Information about safety, health and environment should be displayed in the tanneries.
3. Use of safety items such as face protective shields, acid resistant gloves, aprons, masks may be strictly enforced.
4. Sequential washing instead of continuous washing may be used to conserve water. This will lead to significant water saving and to a much reduced hydraulic load for the effluent treatment plant.
5. Environmental friendly chemicals may be used e.g. replacing sulfides and surfactants with enzymatic products.
6. Avoid the formation of hydrogen sulfides inside the tanneries by improving the drainage system.
7. Proper action should be taken to stop the use of tanned solid wastes in the preparation of poultry feed.
8. Chemical recycling should be practiced.

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