WASTEWATER TREATMENT TECHNOLOGY FOR TANNING INDUSTRY

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Summary

The leather industry is a major industry on an international scale and is of significant economic importance. The industry has received criticism on environmental grounds and the tanning industry has been viewed to be a major source of water pollution. Tannery wastes are uniquely identified as an activity generating pollution of mixed character in the sense that both organic and inorganic constituents occur at concentrations higher than other wastes. Tanneries are thus obligated to treat effluent to a level that cause less impact on the environment. The extent of pollution from the various tanning operations in terms of its volume and characteristics, together with the various treatment methods applicable are discussed. Collectively they could form the basis for a state-of-the art technology for the treatment of effluents from the tanning industry.

1. Introduction

1.1 Tanning: Historical Developments

Tanning is the process of transforming animal skins (a natural renewable resource) to leather (a market material used in the manufacture of a wide range of products). Tanning is claimed to be the second oldest profession in the world. In ancient times, tanning was considered as a noxious trade. However the industry has evolved with time. The leather industry is now recognized as a major industry of great economic importance on an international scale producing a host of products in one of the world's finest natural materials. Tanning industry is sometimes criticized on environmental grounds, although the only other viable alternative of dumping the putrefying hides and skins can be more hazardous and can cause even more severe environmental damage.

1.2 Tanning Industry: A Global Outlook

Leather is a globally acclaimed product and there is an ever increasing demand for leather and its related products. The current trade value of the leather industry is estimated to be approximately US$ 70 billion per year. The industry in total produces about 18 billion square feet of leather a year, with developing countries producing over 60% of the world's leather. About 65% of the world production of leather is estimated to go into leather footwear. Its major expansion has taken place in developing and newly industrialized countries rather than in developed economies. In developing and newly industrialized countries solid waste and wastewater treatments are not state of the art and there is a high labor content to the processes involved in the conversion of hides and skins into leather. The United States, Germany, and other European countries remain major importers of leather products. Countries such as China, India, Thailand, and Indonesia dominate the export of leather and leather products.

2. Tanning Process

The technology for the production of leather is largely conventional having become popular amongst the tanners. To date, there are only two processes i.e. vegetable

tanning or East India tanning (EI) and chrome tanning. In vegetable tanning, tanning agents such as bark from the quebracho or babul trees or wattle extract are used while in chrome tanning, chromium is used. The main protein of the skin, collagen reacts with the polyphenols in the plant materials or chromium. In vegetable tanning, the collagen reacts with vegetable tannins via hydrogen bonding to form a stable matrix. In chrome tanning, diffusion of chromium (III) salts into the skin matrix at pH 3.5-4.0 leads to irreversible binding of Cr (III) to the collagen protein through coordinate covalent bonding. Vegetable tanning process is employed for producing sole and other heavy leathers whereas chrome tanning is used for producing light weight leathers like shoe uppers and upholstery leathers. The chrome-tanned hides or skins are called wet blue in the tanneries. About 90% of the leather produced globally is by chrome tanning process. The tanning of leather either by EI tanning or chrome tanning has common units of operation in conversion of raw material into an intermediate form from where specific products can be developed. Leather process may be classified into: (1) Raw to finish, (2) Raw to E.I., (3) E.I. to finish, (4) Raw to wet blue, (5) Wet blue to finish and (6) Crust to finish.

During leather processing, the hides and skin undergoes a series of pre-tanning, tanning and post-tanning operations. Water is an input material used in large quantities most if not all the processes of tanning and finishing of the animal skins and hides. The running of process equipment and floor washing are inevitable operations in any tannery. The quantity of water used in processing a kg of hide/skin is about 30–35 litres and varies with process (Table 1).

Sl. No.	Type of process	Volume of water used
1.	Raw to finish	40 - 45 l/kg of raw weight
2.	Raw to E.I.	25 - 30 l/kg of raw weight
3.	E.I. to finish	50 - 60 l/kg of E.I. weight
4.	Raw to wet blue	25 - 30 l/kg of raw weight
5.	Wet blue to finish	20 - 25 l/kg of wet blue weight
6.	Crust to finish	10 - 15 l/kg of crust weight

Table 1 Volume of water used for different processes

The other inputs in the form of chemicals are introduced into processes as desired. The initial processes are basically to remove the impurities, which adhere or attach to the raw materials during flaying, and pretreatment for controlling moisture and pests and microbes. The impurities are picked up during transport and handling in markets and tanneries. The pretreatment is to remove the salt, dirt, blood, meat, bones, etc., and to remove the salt along with rehydration of the raw materials. This is in other words to bring the material to their natural form. Processes are classified into two forms depending upon the functional needs of the various operations. They are known as “beam house operation” and “tanning operation” in a tannery processing raw materials to obtain finished leather.

2.1 Beam House Operations

2.1.1 Trimming and Desalting

The wet salted skins/hides are drawn from storage yards to the operational floors either manually or mechanically. The first operation is desalting by flinging the hides and skins in air and brushing them by mechanical desalters. The collected salt is stored for disposal or reuse within the tannery. The hides and skins undergo rehydration during the curing process. To facilitate the absorption of chemical additives in solution, the raw materials have to be rehydrated through the process of "soaking".

2.1.2 Soaking

The soaking is carried out in two/three stages with respect to removal of salt along with other impurities from raw materials by rationing water and regulated withdrawal of salt from salted hides/skins. The soaking process not only helps to bring the hides and skins to the original form but also removes blood, dung, dirt, and soluble proteins like albumin and globulin. Pits or paddles are used for soaking. At every stage, 200-400% of water by weight of the skin or hide is used. Also 0.1% preservative (biocides) and 0.2% wetting agent (detergents) are added at the first stage itself. At the end of soaking process, a sizeable percentage of salt and other impurities remain in the spent soak liquor.

2.1.3 Liming

The liming of the salt free and rehydrated material is carried out in two stages primarily to swell the hide substances and loosen the hair roots. Copious amount of water is used (300-400% w/w). Lime and sulphide of sodium in solution at fixed strength are added to water held in the pits or the trough which have mechanically operated paddles. The stock of raw materials is charged to pits or troughs and steeped over a time. The loosened hair and the spent lime and sulphide are removed by washing with plain water. In case the hair of the goat or sheep is to be saved, the paste of lime and sulphide is applied on the flesh side and aged for some time to facilitate the easy removal of the hair.

2.1.4 Reliming

Reliming is carried out in the same manner as liming in either pits or paddles mostly with 300-400% water and lime. Soda ash or sodium hydroxide is used in small quantities to hasten swelling to obtain better opening up of collagen fibre in a shorter period. After the reliming is complete, the goods are fleshed and scudded to remove short hair and dirt. The relimed and defleshed hide/skin is called pelt.

2.1.5 Deliming

The purpose of deliming is to eliminate the alkalinity caused by lime on the collagen. Water charged at the rate of 200% w/w and 1% NH_4Cl in solution is usually sufficient to eliminate residual alkalinity. Also, 2-3% degreasing agents are added to remove

grease from the pelts. Besides, 1% bating enzyme is added to remove the fats. About 200% of water is used for washing.

2.2 Tanning Operations

2.2.1 Pickling

The popular practice in India is to manufacture leather for shoe uppers, garments, gloves, etc. The quality of leather for this purpose is defined in terms of softness, suppleness and strength. In order to attain these qualities, it is necessary to pickle the pelt with acid and salt. Pickling is the process in which sulphuric acid and common salt (NaCl) are added to the delimed pelts in order to facilitate tanning. Pickling is carried out in drums. Salt (10%), sulphuric acid (1%) and formic acid (0.5%) are added together to the float (100%). The pH of the mixture is in the range 3.0-3.5 for complete pickling for vegetable tanning operations and 2.8-3.2 for chrome tanning operations.

2.2.2 Chrome Tanning

The pickled skin/hide partially freed from pickle liquor is tanned in drums. Basic chromium sulphate (8% w/w) is used as tanning agent. Sodium bicarbonate (1% w/w) and sodium formate (1% w/w) dissolved in water (50%) are used to basify the content to the pH range of 3.8 - 4.0. Preservative (0.1%) and water (100%) are added and tumbled. The tanned pelts are called wet blues. The wet blue skins/hides are sammed (dewatering) in sammying machine. The sammed skins are shaven to the required thickness in the shaving machine. Based on the shaven weight, water and chemicals are used for subsequent processes.

2.2.3 Rechroming

The shaven skins/hides is washed with water (200%) and tanned with basic chromium sulphate (5%) in water (150%). Sodium formate (1%) and sodium bicarbonate (1%) are used in the process to facilitate good fixing of the chromium.

2.2.4 Neutralisation

The objective of neutralisation is to remove excessive acid present on the leather and also to condition leather for subsequent dyeing and fat liquoring operation. The rechromed wet blues are washed with water (200%). The washed wet blue is neutralised by the addition of formate (1%) and bicarbonate of sodium (1%). The final pH of the pelt lies between 4.8 and 5.3.

2.2.5 Dyeing, Fat Liquoring and Retanning

The neutralised skins/hides are washed with water (200%). Hot water is used for dyeing and fat liquoring. Water (200%) at 60°C and appropriate dye (4%) are mixed together and added to the chrome tanned skins/hides. Subsequently fat liquor (12%) is added to upgrade the quality. Formic acid is used to fix the dyes and fat liquor. The dyed leather is at times tanned by the addition of synthetic tannins. The purpose of the

retanning is to obtain special quality like fullness. The dyed leather has to be washed with plain water and dried before they are taken to finishing yards.

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Biographical Sketches

R.A. Ramanujam, received his Bachelor of Technology (Chemical Engineering) in 1975, Master of Technology (Chemical Engineering) in 1977 from A.C College of Technology and Ph.D (Environmental Engineering) in 2002 from the University of Madras. He has been working as a Scientist in the Department of Environmental Technology of Central Leather Research Institute (CLRI) since 1991. Before joining CLRI, he was working for about 14 years in private industry and National Council for Cement and Building Materials, Government of India in the field of Environmental Engineering. His areas of specialisation are environmental impact assessment for industrial complexes, environmental management system, environmental auditing, anaerobic treatment of solid and liquid wastes, industrial wastewater treatment and disposal, etc. He has undergone training in the field of Air Pollution Control with reference to particulate emission abatement utilising fabric filter in M/s Fuller Co., Bethleham, PA, USA under UNIDO programme and specialised in design, operation and maintenance of fabric filter, Environmental Impact Assessment and Auditing in the University of Bradford, UK under Technical Cooperation Training Programme of Colombo plan and specialised in Environmental Impact Assessment and Auditing procedures, and Biomethanation and waste management at AEA Technology, National Environmental Technology Centre, Culham, Abingdon, Oxfordshire, UK. He is an Associate member of Indian Institute of Chemical Engineers, Life member, Indian Association for Environmental Management and Active Member, Indian Environmental Management, Fellow of Institution of Engineers and a faculty in the Department of Leather Technology, Anna University. He is project leader of UNIDO-UNDP-GEF and Ministry of Non-conventional Energy Sources, Government of India supported programme for leather and allied industries in India for the development of appropriate technology for the management of solid wastes and recovery of energy, and an active consultant for several projects on Environmental Impact Assessment (EIA) and Environmental Audit (EA) for chemical industries, refineries, petrochemical industries and tanneries in India and for establishment of leather complexes in India. He has published several technical papers in reputed journals.

R. Ganesh, received his B.Sc degree (Applied Sciences) from the University of Madras in 1994 and M.Sc degree (Applied Chemistry) from the Bharathiyar University in 1996. He is currently Senior Research Fellow and a doctoral candidate in the Department of Environmental Technology of Central Leather Research Institute (CLRI), Chennai, India. His research interests are physico-chemical treatment, carbonaceous oxidation, nitrification, denitrification, respirometry-based studies of wastewaters, modeling of wastewater treatment systems, anaerobic fixed-bed treatment of wastewaters and solid waste management of tannery, vegetable wastes by biomethanation processes. He has undertaken an eight-month research training programme in Institut National de la Recherche Agronomique (INRA), Narbonne, France. He has several publications in national and international journals and is a reviewer for international journals.