Water Management in Leather Industry

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Leather industry, like paper and textile industries, consumes large quantities of water. Such excessive usage, resulting from adoption of traditional processing methods and equipments, lead to acute water availability and effluent treatment problems. Presently, about 30 billion litres of water is being used by this industry annually. A systematic study made at CLRI to reduce the excessive usage and further minimise water consumption in leather processing through optimisation and recycle and reuse strategies. The role of newer equipments, such as the hide processor and the compartmental drum in minimising water usage in leather processing has also been studied extensively. Most of the protocols standardised at CLRI were implemented at select tanneries in India and Sri Lanka, which resulted in better water management in the leather processing industry. The results of such detailed studies have been incorporated in the paper.

Introduction

Water utilisation by mankind may be divided into three broad categories, agricultural, domestic and industrial. Apparently, there is no dearth of water as 80 per cent of the earth’s surface is covered by water. Even then, the world is heading towards a water crisis because 97.5 per cent of the global water reserve is salt water and only 2.5 per cent constitutes fresh water reserve. Out of the fresh-water reserve, 68.8 per cent is present as glaciers and permanent snow cover, 30 per cent as fresh ground water, and only 0.3 per cent is present in the form of lakes and rivers and 0.9 per cent as soil moisture. The world population also doubled between 1940 and 1990 and so did the per capita water consumption from 400 to 800 m³. The World Bank has, recently estimated that the demand for water could be expected to grow by over 650 per cent in the next three decades.

In spite of India being one of the wettest countries in the world, with average annual rainfall of about 1200 mm, it is ironic that drought conditions and floods are witnessed simultaneously year after year. A major portion of 400 Mham of rainwater is lost by way of seepage, evaporation and run off to sea and she is able to utilise only 38 Mham, nearly one-tenth of the total rainfall, with irrigation accounting for 92 per cent of it, leaving a mere 8 per cent for domestic and industrial use. Thus, the composition between human and industrial demands comes under sharp focus of the water conservation efforts. The major responsibility, however, falls on the industry.

Water Usage in Leather Industry

Water is an important medium in leather processing. Almost all the unit operations of leather making use water as a processing medium. Nearly 40-45 L water/kg raw-hide or skin is used by tanneries for processing finished leathers. With annual raw-hide or skin processing of the order of 690,000 tonnes, total water requirements for the industry approximate 30 billion litres. Such huge volume of water, used in leather processing, poses two problems, viz, availability of water in required quantity and the treatment of effluents thus generated, as almost entire quantity of water used in processing is let out as effluent. Apart from pollution load, the huge quantities of effluent require large investments on effluent water-treatment plants.

Conventional Leather Processing Technology

The leather processing activities can be broadly categorised into Beam house, Tanning and Post-tanning operations.

Beam House Operations

Soaking, liming, deliming-cum-bating and pickling are the unit operations under this category which are briefly discussed below:
Soaking

Salted hides and skins constitute major raw material for processing by the industry; the salt content varying between 25-35 per cent by weight. The first operation in leather processing is to reverse the changes brought about in curing and bring hides and skins back to the original condition as they were flayed. Generally, soaking is done to remove salt absorbed by hides and skins during curing, and, also, to rehydrate the skin. Other materials like dirt, dung, blood and some of the inter fibrillar proteins are also removed during soaking. In soaking, 6,000-9,000 L water/h hide is used.

Liming

Liming — is carried out in two stages—in the first stage, hair or wool and flesh are loosened which facilitate their mechanical removal; and in the second stage, the hide matrix structure is opened up which promotes diffusion of chemicals in subsequent operations. The first stage is designated as dehairing operation and the second is termed as reliming. In the dehairing operation, a paste, containing lime, sodium sulphide and/or an enzyme, is used while for reliming, 3-3.5 per cent lime solution is used. Water to the tune of 4,000-6,000 L/t hide is used in liming. After reliming, the hides are fleshed and weighed. The weight thus obtained is termed as pelt-weight and it forms the basis of other operations up to tanning.

Deliming-cum-bating

Deliming is carried out using ammonium chloride or ammonium sulphate to neutralise and remove the lime from pelt. The end-point is ascertained with phenolphthalein, and absence of pink colour indicates absence of lime. Treatment of delimed hides with enzymatic preparations (i.e., bates), for removal of scud, short hair and to improve grain characteristics is called bating. Completion of bating is ascertained by retention of thumb impression or squeezing out the air through the skin. Water, at the rate of 4,500 to 5,000 L/t hide, is used in deliming and bating.

Pickling

The process of conditioning delimed and bated pelts for chrome tanning is called pickling. Typically, pelts are treated with 10 per cent brine solution initially. Then sulphuric acid is added in feeds to attain equilibrium cross-section pH of 2.8-3.0. In pickling, 800-1,000 L water/h hide is used.

Tanning

Tanning basically aims at stabilisation of hide, which is obtained through treatments with a variety of agents like vegetable tanning materials, mineral tanning salts, synthetic tannins, aldehydes, etc. The choice of tanning method and the agent depends chiefly on the properties required in the finished leather, cost of materials and the type of raw material. The most common tanning systems used are vegetable, chrome or a combination of both. As more than 80 per cent of finished leather, produced in India, is through chrome tannage, the paper is oriented towards technologies concerned with processing of such leathers.

Conventionally, chrome tanning involves treating pickled pelt with basic chromium sulphate, using water as the medium. After ascertaining sufficient penetration of chromium by examining the cross-section, the pH of the tanning bath is raised to 3.8-4.0. Water in the range of 1,500-2,000 L/t pelt is used in tanning process.

Post-tanning Operations

Post-tanning technology covers wet processes that are performed on tanned leathers and consists of rechrome tanning, neutralisation, retanning, dyeing and fatliquoring.

Rechrome Tanning

The levelled chrome tanned hides are treated with basic chromium sulphate in order to equalise chromium in tanned leathers, and the process consumes water between 2,000-3,000 L/t chrome tanned leathers processed.

Neutralisation

The acidity of leather is neutralised and, with this, the charge characteristics of leather are also altered. The surface charge of chrome-tanned leather, which is highly cationic, is reduced during neutralisation to less positive nature so that the uptake of anionic retanning agents, dyestuffs and fat liquors could be regulated. Thus, neutralisation makes it possible to achieve a better and uniform distribution of processing agents during subsequent processing. Neutralisation is carried out in three stages, viz., washing, neutralization, and again washing, requiring 5,000 to 6,000 L water/t tanned leather.

Retanning

By nature, a chrome-tanned leather lacks fullness due to lower molecular weight of chrome complexes. Hence, chrome tanned leathers are always subjected to retanning.
The type of retannage and amount of retanning materials vary depending upon the characteristics desired in the final leather. Various types of retanning materials are available for the purpose, e.g., vegetable tannins like wattle, quebracho, replacement/retanning syntans which are phenol-formaldehyde condensates, aldehyde retanning agents, acrylic syntans and resin syntan based on melamine formaldehyde condensate. A combination of retanning materials is chosen depending upon the final quality characterises desired in finished leather.

Dyeing

The process of dyeing is considered in relation to retanning and fatliquoring, as all these materials are anionic in nature, and one can act as a regulator of the other. Mostly anionic dyestuffs, and to a small extent cationic dyestuffs, are used in leather dyeing. The final physical properties required in the leather such as light fastness, rub fastness, resistance to solvents, perspiration resistance, etc will determine the choice of dyestuffs.

Fat liquoring

It lubricates fibres and consequently softens leather. The affinity of a fat liquor to a tanned leather and its efficiency in lubricating fibres is dependent on factors like nature of the fat liquor, nature of the substrates, the stage of application, and the type of finished leather. Fat liquors are anionic in nature and they are based on vegetable oil, marine oil and synthetic hydrocarbons; although a small percentage of cationic fat liquors are also used. Normally, retanning, dyeing and fat liquoring are carried out together. The water requirements for these operations has been estimated between 2,500-3,500 L/t tanned leather. Typical water requirements for various unit operations are given in the following flow diagrams.

Water requirements for pre-tanning and tanning operations

Total water required in pre-tanning operations, including 40 per cent towards spillage and hose keeping: 44,000 L, that is, 34 L/kg hide.

Basis: Chrome tanned leathers corresponding to one tonne raw hide

Total water required in post-tanning operations, including 40 per cent towards spillage and housekeeping: 6,000 L, that is, 6 L/kg hide.

Better Water Management: Proven Strategies

CLRI has evolved a number of water management approaches, most of which have been commercially tested and practiced by select tanneries in India and Sri Lanka. The strategies adopted for water management include

- Recycling of sectional process liquors,
- Recycling - direct reuse of water in less critical processes,
- Low float processing, and
- Increased volume control

Recycling of Individual Process Liquors

In many unit operations of leather processing copious amount of water is used, as a result, large quantities of water emanate as sectional waste streams offering a good scope for recycle and reuse in the same or other suitable operations. However, appropriate replenishment of water and chemicals will be required. Recycling of soak liquor becomes necessary due to the need to reduce total water use in leather processing. As primary or first soak liquor contains rather large amounts of dirt and other foreign matter, recycling of this stream is a challenge calling for removal of dirt and all the foreign matter, followed by sterilisation through irradiation methods prior to reuse. On the other hand, the second and third soak water can be recycled for successive batches without much problem. Counter current soaking method can be employed with advantage as shown in Figure 1. This technique provides savings of 60-65 per cent of the water generally used in soaking operation. In this method, hides or skins move in one direction while water flows in the counter direction. With 9 L/kg of hide processed being used in conventional soaking the counter current soaking technique leads to a saving of nearly 6 L water per Kg hide processed. The physico-chemical properties of leathers obtained by counter current soaking system were found comparable with that of conventionally processed leathers.

Liming

Liming operation utilises large quantities of water. In this operation, recycling once for the next batch reduces requirements of water. Even the counter current method similar to that employed in soaking can be used which ensures reduction of water requirements up to 60 per cent of total water otherwise necessary in this unit op-
Recycling Direct Refuse of Used Water to Less Critical Processes

A number of recycle and reuse strategies were evolved for the various unit operations and their use have been established at the commercial scales. To mention a few, water used in washing of fleshed pelt could be reused for supplementing water required for reliming in subsequent batches. The deliming spent liquor could effectively be used for washing fleshed pelts in subsequent batches and the wash liquor after deliming could be used for deliming in subsequent batches. A number of such recycling of spent liquor is a commercial reality. This scheme is shown in Figure 2.

Similarly, the washing and neutralisation spent liquors offer scope for recycle and reuse within these operations as shown in Figure 3. The engineering requirements of such a system, while not being over sophisticated, may make it difficult to implement in some of the existing tanneries, but could easily be incorporated in a new project. The major requirement, in addition to collection sump(s) is the incorporation of a bifurcated drain whereby flow from any given unit operation could be directed either to

1. The recycling networks or
2. Normal effluent sewer

Bifurcation of drain and collection system would entail additional supervision to ensure the discharge of individual floats into correct outlets.

It may be argued that the installation of a recycling network, merely to save some 25-50 per cent of water usage, is unlikely to prove economical, except in ultra-arid areas where water is both limited and expensive. However, when simple water recycling is coupled with recycling of unused chemicals for carrying out the same unit operation with appropriate replenishments then economic benefits may become significant.
Water requirement for post-tanning operations

Figure 1 — Counter current soaking

Low Float Techniques

The utilisation of short floats leading to savings in water consumption and processing time in many processes, effect appreciable amount of chemical input savings, due to higher effective concentration and increased mechanical action. With regard to water utilisation, it should be emphasised that wherever possible drums should be employed in place of paddles and pits, which utilise 300-1000 per cent floats, although it must also be recognised, that paddles and pits are essential in certain processes. Studies have also been made to optimise the input of water and chemicals in a number of unit operations using conventional wooden drum. It was found that deliming could effectively be carried out even with 0-0.25 L/kg of water against 1.0-1.5 L/kg in conventional methods. Similarly, it has been established that more than 50 per cent water input could be minimised in pickling process.

Figure 2 — Water management plan for beam house and tanning operations

Hide processor and compartmental drum are the two newer type of processing vessels that have gained significance in tanneries abroad and the same can be effectively used in Indian tanneries for better water management. Extensive studies have been made using hide processor and compartmental drums for leather processing; some of the salient results are given below.

Hide Processor

Based on the design of the equipment, the advantages of the hide processor are

- gentle mechanical action, consequently better grain characteristics of final leathers.
- pumped recirculation system offering better scope for lower liquor to hide ratios and hence less effluent.
- easier loading and unloading of hides
- lower power requirements due to reduced starting torque.
- Less space requirements

However, when hide processors are used longer processing time is required. In order to monitor the efficiency of hide processor in the operation of deliming.
the hides were cut into sides and the rights were processed in the hide processor with the corresponding left sides being processed in the drum. After deliming both the sides were pickled and chrome tanned in the conventional wooden drum.

By conducting a series of experiments, varying the float and the amount of deliming agent used, it was found out that savings to the extent of 40 per cent in water could be obtained using hide processor in deliming, without adversely affecting the characteristics of the finished leathers.

Similar to deliming, optimisation of water input in pickling operation using hide processor has been done. As mentioned earlier, the hides were cut into sides and rights were pickled in hide processor and the lefts in the conventional drum. The sides were then chrome tanned in the conventional drum. The savings in chemical and water input were nearly 30-35 per cent with the use of hide processor.

The chrome tanned leathers obtained in the hide processor were comparable with control with respect to both chrome fixation and hydrothermal stability. The leathers also had uniformity in colour and were smooth grained in both the cases. Further, this system also offers a scope for recycle and reuse of pickle liquor with appropriate replenishments.

In order to combat poor exhaustion problems, attempts were made to develop low float system with gentle mechanical action of the hide processor. As the role of salt in tanning is mainly to prevent acid swelling, effective concentration gradient plays a vital role and the amount of salt used can be reduced considerably coupled with the reduced quantity of water used for tanning in the hide processor.

By varying total float used for tanning, keeping the amount of mineral oxide offered constant (1.5 per cent of pelt) a series of experiments were carried out to explore the possibilities of savings in water and chemical
input in chrome tanning. The wet blue leathers were analysed chemically for fixed chromium oxide and the shrinkage temperature of leathers were also determined. The analytical data is given in Table 1.

Though the time required for penetration of chrome is slightly high when hide processor is used, there is considerable improvement in fixation of chromium for the same amount of chrome offered. More significantly, the wet blue from the hide processor was fuller in substance with smooth grain and uniformity in colour in contrast to the wet blue with a tendency of drawn grain and non-uniform colour of leathers obtained from the drum with reduced float.

Further, hide processor offers better scope for adopting the high chrome exhaustion techniques like use of high temperature, recycling etc. due to inherent design of the equipment.

**Compartmental Drum**

The compartmental drums are usually made of stainless steel and consist of a perforated cage drum segmented into two or three compartments by radial shelves i.e. in an ‘S’ or ‘Y’ formation rotating in an external casing. The bottom half of the casing holds the float and is fitted with sluice valves, heating elements, temperature and pH probes etc. Each compartment is fitted with a door and can be loaded and unloaded separately, the total load being divided equally between compartments. During operation, the skins tumbling within their particular compartments are being immersed in the float held in the bottom of the casing and during the top half of the rotation, the float drains off. Apart from giving a mere balanced load, draining the float without blockage is facilitated. Though compartmental drums were originally used as dyeing vessels, it can be used for most processes, which employ sufficient float to fill the peripheral gap between bottom casing and cage. Based on the design, the advantages claimed for the compartmental drum are:

- gentle mechanical action
- elimination of tangling, particularly of lighter hides
- occupies less space
- due to balanced load, low starting torque and hence reduced power consumption
- lends itself to process automation
- possible use of low float system, hence low effluent
- significant savings in chemicals (because of greater exhaustion)

With a view to utilise these special features, a series of experiments were carried out during retanning, dyeing and fat liquorising of cow hides with a view to studying the efficiency of the compartmental drum in saving chemicals and water input. The quantity of retanning agent and dye offered was reduced, however, keeping the concentration of both the chemicals same as in the wooden drum.

The results indicated savings in water and chemical input to the extent of 40 per cent in retanning, dyeing and fat liquorising operations.

Visual assessment of leathers thus processed showed that in spite of a reduction in the amount of retanning materials and dyestuffs offered in compartmental drum, finished leathers were comparable with the control made in the wooden drum. One major advantage of the use of the compartmental drum for processing is the smooth and tighter grain character of leathers, which could possibly be due to a gentle mechanical action, while the leathers processed in the wooden drum even with a larger float showed looseness of grain.

Physical testing of the crust leathers showed very little variation in the strength characteristics irrespective of the reduced input of water and chemicals.
Table 2—Water requirement (L/kg hide) pattern in various operations in leather processing

<table>
<thead>
<tr>
<th>Operation</th>
<th>Conventional technology, L/kg hide</th>
<th>Improved process technology (optimisation and recycling), L/kg hide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soaking</td>
<td>6.0 - 9.0</td>
<td>2.5 - 3.0</td>
</tr>
<tr>
<td>Liming</td>
<td>4.0 - 6.0</td>
<td>2.0 - 2.5</td>
</tr>
<tr>
<td>Deliming</td>
<td>4.5 - 5.0</td>
<td>1.0 - 1.5</td>
</tr>
<tr>
<td>Pickling</td>
<td>0.8 - 1.0</td>
<td>0.5 - 0.8</td>
</tr>
<tr>
<td>Tanning</td>
<td>1.5 - 2.0</td>
<td>0.5 - 1.0</td>
</tr>
<tr>
<td>Rechrome tanning</td>
<td>0.7 - 1.0</td>
<td>0.7 - 0.8</td>
</tr>
<tr>
<td>Neutralisation</td>
<td>1.7 - 2.0</td>
<td>0.7 - 1.0</td>
</tr>
<tr>
<td>Retanning, dyeing and fat liquoring</td>
<td>0.8 - 1.2</td>
<td>0.7 - 1.0</td>
</tr>
<tr>
<td>Washing and spillage</td>
<td>11.0 - 13.0</td>
<td>5.0 - 6.0</td>
</tr>
<tr>
<td>Total</td>
<td>30.0 - 40.2</td>
<td>12.7 - 17.6</td>
</tr>
</tbody>
</table>

In majorit y of tanneries only about 70 per cent of water consumed is related to actual process requirement. The balance of the water consumed appear to be due to extensive running water washes, overflowing vessels, continually running pipes and more frequent washing of floors and drums.

Reduction of overuse in this area, while cost-effective, would necessitate a serious worker-training programme, coupled with installation of water flow meters or less sophisticated spring controlled valves. Considerable savings have been obtained with the introduction and control of simple ‘housekeeping’ rules and equipments.

The age-old tannery system of running water rinsing, whereby the leathers are washed with running water for 15-20 min, is one of the major tannery wastages of water. Work at many tanneries showed that 50 per cent of total water utilised for the operation could be saved by resorting to batch washes. Such batch washing should also yield a product of greater uniformity.

Summing up

Resorting to control measures and recycling, reuse strategies lead to significant saving, to the tune of 65-70 per cent in water inputs required for leather processing. Use of newer equipments provides additional benefits. Given the quantum of processing around 2300 tonnes per day the savings in water required amount to 4600 kL per day when water-reducing strategies are employed. The saving in water input accrued by different approaches is given in the Table 2. There is a need for comprehensive approach to water management in tanneries as shown in Figures 2 and 3. It is essential to mention that many tanneries are already employing various combinations of the approaches mentioned in this paper. Efforts are also being made to reuse treated effluent for certain operations in leather processing again with varying degrees of success.

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3. Industrial pollution reduction programme at Sri Lanka (by Central Leather Research Institute, Adyar, Chennai for UNIDO)