

USE OF SEAWATER IN LEATHER PROCESSING

by

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ABSTRACT

The leather industry is one of the major consumers of significant quantities of water. There is an urgent need for tanners to conserve water and effect process modifications leading to minimizing the consumption of water, which is currently recognized and adopted to varying extent. As the monsoon fails quite often and the underground water is drastically decreasing, recourse to suitable technologies become essential, especially in tropical countries. Need for specific quality of water for different operations do pose restrictions on use of water from different sources. This paper deals with a study made on use of seawater for leathers processing. The results indicate that pre-treated seawater could be used for select operations in leather processing without any impairment in the leather quality.

INTRODUCTION

Leather making involves a large number of process steps that utilize water as medium. Nearly 40-45 L of water per kilo of raw hide or skin are being used by tanneries for processing finished leather¹. Such a huge volume of water used for processing poses problems like availability of water in required quantity, and quality. Acceptable composition of water² for use in different unit operations by the tanning industry is given in Table I

Nearly 80% of the earth's surface is covered by ocean. About 98% of water available on land is salty and the global fresh water contributes only 2%. Out of this 69% is present as glaciers and permanent snow cover, 30% as fresh ground

water. Only about 0.5 percent of the fresh water reserve is present in the form of lakes and rivers and about 0.5 percentage as soil moisture. The world's population is increasing drastically and in particular doubled between 1940 to 1990, and the per capita water consumption has also increased considerably. The need and demand for water will keep increasing for human consumption and the water availability for industries will go down and invariably they will be forced to look for water sources other than underground water. However, water from most of the other sources is saline in nature. Among the desalination processes, the most advanced are multistage flash distillation, electro-dialysis and freeze separation, the last option has been identified as the least expensive and most reliable of these processes.³ For example, Northern Chile possesses a dry, transparent atmosphere giving rise to large temperature drops due to evaporative and radiative losses and this makes it possible⁴ to freeze salt water placed under the open sky as a natural freezing process. Most of these processes are directed towards solving drinking water-related problems. Use of both treated or untreated seawater is common in some chemical industries where the process is less sensitive to dissolved solids, in particular to temporary, and permanent hardness.

As the temporary and permanent hardness in water is bound to affect some of the process steps in leather processing,⁵ seawater is treated with some of the common chemicals like calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and hydrochloric acid (HCl) for reduction of hardness and the treated sea water is taken for experiments.

EXPERIMENTAL

Seawater from the Bay of Bengal was taken for the present study. The collected sea water was allowed to settle

TABLE I
General Tolerances for Water Used by the Tanning Industry

Characterstics	Soaking	Liming	Deliming	Dyeing	Vegetable tanning	Chrome tanning
Total hardness, CaCO_3 (mg/l)	--	--		30	30	300
Carbonate Hardness, CaCO_3 (mg/l)	--	50	50	--	--	--
Chlorides (as Cl, (mg/l))	--	--	--	--	500	500

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overnight and on the next day was treated with 0.04% weight by volume calcium hydroxide (AR grade) and mixed thoroughly in order to precipitate the substance leading to temporary hardness (bicarbonates) and allowed to settle.

Next day the water was carefully siphoned out and treated with sodium carbonate (AR grade) 0.05 % weight by volume and mixed thoroughly and left overnight allowing the particles to settle whereby salts contributing permanent hardness precipitated out. On the third day after siphoning from the top, the water was treated with sodium hydroxide (AR grade) 0.05% weight by volume to remove magnesium salts as hydroxides and left overnight. The treated water was

carefully siphoned on the fourth day so that the jelly mass was not disturbed and the siphoned water was neutralized to the pH of 6.5-7.0 using dilute HCl. This treated water was used for leather processing.

Seawater's constituents before and after the treatment were analyzed using atomic absorption spectrometer, chloride ions were determined by titration with silver nitrate solution, and the total solids determined by gravimetry.

The process, as given in Table II, was adopted to process cow upper leather and goat upper leather using treated sea water. Trials were also conducted with water from conven-

TABLE II
Process Adopted for Cow Hides and Goat Skins.

Process	Cow upper leather	Goat upper leather
Soaking I	Water 300 % Wetting agent 0.5%, -- 30'	Water 300% Wetting agent 0.5%, -- 30'
Soaking II	Water 300% Preservative 0.1% Wetting agent 0.5%, --left overnight	Water 300 % Preservative 0.1% Wetting agent 0.5%, --left overnight
Next day Washing	Water 200%	Water 200%
Liming	Water 150% Lime 10% Sodium sulfide 2%, --Left for 3 days in pit	Water 25% Lime 10% Sodium sulfide 3% Wetting agent 0.5% --Paint prepared and applied on flesh and left overnight. Next day the hair was removed over beam. Reliming: Water 200% Lime 5%--Left for 1 day
The limed pelts were fleshed and taken for washing		
Washing	Water 200%, --10 min	Water 200%, --10 min
Delimiting	Water 150%. Ammonium sulfate 2% Bate 0.5%, --Run for 2 h	Water 150% Ammonium sulfate 1% Bate 1%, --Run for 1 h.
Washing	Water 100%, --10 min	Water 100%, --10 min
Pickling	Water 80% Sodium chloride 8%--Run for 10" Formic acid 1%--Run for 10" Sulfuric acid 1.5%, (4 x 15")	Water 80% Sodium chloride 8%--Run for 10" Formic acid 0.5%--Run for 10" Sulfuric acid 1%, (4 x 15")
Next day the pelts drummed for 30". pH at cross section adjusted to 2.8-3.0. Then 50% of pickle bath drained.		
Chrome tanning	Basic chromium sulfate 8% (2 x 30") Cationic fatliquor 1.0%(10") Sodium formate 1% Sodium bicarbonate 2% (3 x 5" +30") pH 3.8 - 4.0	Basic chromium sulfate 8% (2 x 30") Sodium formate 0.5% (10") Sodium bicarbonate 1% (3 x 5" +30") pH 3.8 - 4.0
The wet blue skins/hides were shaved to 1.0 mm thickness		
Washing	Water 200% (10")	Water 200% (10")

TABLE II (Continued)

Neutralization	Water 200%	Water 100%
	Sodium formate 0.5%, --10 min	Sodium formate 0.5%,--10 min
	Sodium bicarbonate 1.5%(3 x 10" +30")	Sodium bicarbonate 0.5%(3 x 10" +30")
	pH 5.0	pH 5.0
Washing	Water 200%(10")	Water 100%(10")
Dyeing and fatliquoring	Water 200%	Water 100%
	Ammonia 1%(10")	Dye 2%(20")
	Dye 2.0%(30")	Fatliquor 10%(30")
	Fatliquor 14%(45")	Syntan 8%(45")
	Syntan 12%(45")	Formic acid 1.0%(3x5" +20")
	Formic acid 1.0%(3x5" +20")	

Values given in () are chemical addition time and process time in minutes

tional source (bore well) for comparison of quality and properties and termed as control.

RESULTS AND DISCUSSION

The Table III shows the effect on sea water composition from each chemical treatment. While sodium ion concentration has increased after the treatments, that of magnesium and calcium ions have decreased. There is not much change in the case of chloride ions by the treatment system followed. Although the reduction in total solid content was only 0.5% approximately, water obtained after this treatment had much less total hardness and hence could be used for leather processing.

Sampling of leather for physical and chemical analysis was made as per standard methods(IUP 2 :1968) (IUC 2: 1965). The physical and chemical properties were determined as per standard procedures (ISO methods for physical testing and IUC methods for chemical analysis) and the assessment of leather processed using this water are given in Tables IV, V, and VI. These results shows that the leathers processed with treated sea water were comparable to the leather processed using borewell water. Hence, it can be concluded that seawater offers a good possibility to serve as medium of processing for most of the leather processing steps where by the strain caused by this industry on under-

ground water can be minimised. However the experimental results presented here are based on sea water collected from a particular coast in a particular season. Hence the results can be only indicative and may not be generally applicable to sea water from varying sources. It is believed that by suitable alteration in the suggested treatment procedure, sea water is likely to be made suitable for most of the operations in leather processing.

Earlier studies⁵ have shown that when untreated seawater was used for leather processing, the leather had poor organoleptic properties. The leathers lacked fullness and softness and were poor in appearance. In the present study though the hardness requirements of treated water is not meeting the standards stipulated in Table I, no major changes were observed in the leathers processed using treated sea water.

CONCLUSIONS

The study indicates that sea water can be used for most of the operations in leather processing after suitable pre treatment. This process also demonstrates seawater could be a suitable alternative where water scarcity is very high as the leathers processed using treated sea water was comparable to the leather processed using conventional source of water. The pre-treatment process of seawater and use for leather

TABLE III
Seawater Compositions Before and After Treatment with $\text{Ca}(\text{OH})_2$, Na_2CO_3 , NaOH and HCl

Sample	Total solids (% w/w)	Sodium (g/L)	Calcium (g/L)	Magnesium (g/L)	Chloride (g/L)	Total hardness, as CaCO_3 (g/L)
Borewell water	0.74 ± 0.04	0.14 ± 0.02	0.064 ± 0.02	0.01 ± 0.03	0.2 ± 0.02	0.20 ± 0.02
Sea water	3.03 ± 0.05	8.80 ± 0.20	0.22 ± 0.02	1.05 ± 0.02	13.8 ± 0.1	7.70 ± 0.05
After $\text{Ca}(\text{OH})_2$ addition	2.75 ± 0.01	9.08 ± 0.35	0.19 ± 0.01	1.0 ± 0.01	13.6 ± 0.2	6.80 ± 0.03
After Na_2CO_3 addition	2.67 ± 0.02	9.69 ± 0.15	0.17 ± 0.01	0.85 ± 0.02	13.4 ± 0.1	7.20 ± 0.04
After NaOH addition	2.67 ± 0.05	9.46 ± 0.30	0.19 ± 0.01	0.87 ± 0.01	13.4 ± 0.1	4.80 ± 0.02

(Values are mean and standard deviation from two batches of experiments)

TABLE IV
Physical Properties of Leather Processed Using Treated Seawater(Experiment) and Borewell Water(Control)

Sl. No	Test	Method adopted	Sample	Cow upper	Goat upper
1	Tensile, N/mm ²	ISO 3376	Experiment	21 ± 0.5	16.0 ± 0.5
2	Tensile, N/mm ²	ISO 3376	Control	23 ± 0.5	16.0 ± 0.5
3	Tear strength, N	ISO 3377	Experiment	72 ± 0.6	46 ± 0.6
4	Tear strength, N	ISO 3377	Control	76 ± 0.5	49 ± 0.5
5	Grain crack strength, Load (Kg)	ISO 3379	Experiment	25 ± 0.4	22 ± 0.2
6	Grain crack strength, Load (Kg)	ISO 3379	Control	26 ± 0.3	23 ± 0.5
6	Grain crack strength, Distance	ISO 3379	Experiment	9 ± 0.5	8 ± 0.5
6	Grain crack strength, Distance	ISO 3379	Control	8 ± 0.4	8 ± 0.5

(Average value from two batches of experiments taking one leather from each batch)

TABLE V
Chemical Analysis of Leather Processed in Normal Borewell Water(Control) and in Seawater(Experiment)

Test	Method adopted	Cow upper		Goat upper	
		Control	Experiment	Control	Experiment
Insoluble ash	IUC 7:1965	4.45 ± 0.03	4.11 ± 0.02	4.91 ± 0.08	4.9 ± 0.07
Solvent soluble	IUC 4:1965	7.01 ± 0.05	7.31 ± 0.05	5.01 ± 0.05	4.8 ± 0.08
Chrome	IUC 8:1965	2.72 ± 0.01	2.46 ± 0.07	2.31 ± 0.06	2.2 ± 0.02

(Average value of two sets of experiments batches of experiments taking one leather from each batch)

TABLE VI
Visual Assessment of Leather (Average Value of Hand Evaluation by Three Experts)

Sample	Color	Softness	Tightness	Fullness	Smoothness	General appearance
Leather processed with borewell water (Control)	7±1	6±1	6±1	6±1.5	6±1	6±1
Leather processed with sea water after treatment	7±2	6±1	8±1	7±1.5	7±1	6±1

(Ten point rating: 1 indicates poor characteristics and 10 outstanding characteristics)

processing will largely be dependent on the sea water source. This treatment method was arrived at to basically address the hardness of sea water and will vary depending on regional conditions. This paper only highlights an approach to augment an ever-dwindling precious resource, WATER.

REFERENCES

1. Sunder, V. John, Ramesh, R., Rao, P. S., Saravanan, P., Sridharanath, B., and Muralidharan, C.; Water management

in Leather Industry, *Journal of Scientific and Industrial Research* **60(6)**, 443-450, 2001.

2. Quality tolerances for water for Tanning Industry, Indian standard - IS 4221 (1967).

3. Schroeder, Paul J.; Freezing processes- the standard of the future-an update. *Desalination* **33**, 299-210, 1980.

4. Fourmier, J., Grange, J. L., and Vergara, S.; Water desalination by natural freezing. *Desalination* **15**, 167-175, 1974.

5. Vedaraman, N., Rao, P. G., Raghavan, K. V.; Use of sea water for leather processing. *Leather Research-Industry Get-together 1995*, India.