

Salinity within tannery effluents

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The total global input of bovine hides, sheep, goat and pigskins is nearly eight million tonnes as wet salted weight a year. On this basis, it could be estimated that tanning operations world-wide use some four million tonnes of various chemicals, produce over 300 million m³ of waste water, and about eight million tonnes of solid waste and dewatered sludge.

However, these figures do not include the amount of salt used for preservation. Since possibly a half of the world's production of bovine hides and a great deal of skins are preserved by applying about 40% of salt on green weight, it is evident that hundreds of thousands tonnes of preserving-salt end up in waste water.

Despite frequent deficiencies in design and size of effluent treatment plants (ETPs), when properly designed, constructed and operated, the usual discharge limits for the main pollution load parameters such as BOD, Suspended Solids, Nitrogen, and the major part of COD can be met.

However, in virtually no case are tanneries able to meet the typical limits applicable for chlorides and sulphates, the two main components of the Total Dissolved Solids

Total Dissolved Solids (TDS): the critical unresolved issue

In arid regions, TDS is turning into the main adversary. The tannery clusters in Tamil Nadu, India, and in Italy, is a case in point. Most of the ETPs can produce an effluent in conformity with discharge standards for nearly all parameters. However, the treated effluent is virtually useless or rather potentially harmful due to its high TDS. This is mainly due to the chloride and sulphate content.

So far no cost effective, affordable technology has been developed anywhere to deal with this problem. Tanners, environmental specialists and enforcement authorities are eagerly looking for technically and economically viable options.

Salt as a component of TDS

In a typical tannery effluent the TDS includes carbonates, phosphates, nitrates, residual sulphides, hydroxides, ammonium and dissolved organic matters (which also make part of the BOD₅ and COD).

Ammonium and nitrates are removed through nitrification/denitrification, and the dissolved organic matter is degraded or eliminated in the course of biological treatment. However, the two components causing most difficulties are chlorides

and sulphates.

Moreover, for practical reasons the problem is simplified by referring to anions only (chloride and sulfate). Nevertheless, cations make a significant part of TDS in effluent, and after

Figure 1: Chloride, sulfates and TDS generated in process

Values per ton of raw hide	Water (m ³ /t)	COD (kg/t)	BOD ₅ (kg/t)	TKN (kg/t)	Cl ⁻ (kg/t)	(SO ₄) ²⁻ (kg/t)	TDS (kg/t)
Beamhouse	7/25	120/160	40/60	9/14	120/150	5/20	200/300
Tanning	1/3	10/20	3/7	0/1	20/60	30/50	60/120
Post tanning	4/8	15/40	5/15	1/2	5/10	10/40	40/100
Finishing	0/1	0/10	0/4				
TOTAL	12/37	145/230	48/86	10/17	145/220	45/110	300/520

Based on data by IULTCS/IUE6, year 2002

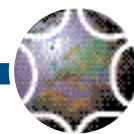
normal treatment this tends to be sodium (Na). Details of TDS, chlorides and sulphates emanating from different stages of processing are given as Figure 1.

At this level of pollution load and on the basis of water consumption/discharge of 30 m³/t, the typical chloride, sulfate and TDS values in the combined tannery effluent are:

Cl⁻ 4 800 - 7 300 mg/l
 (SO₄)²⁻ 1 500 - 3 600 mg/l
 TDS 10 000 - 17 300 mg/l

Figure 2: Material balance of common salt applied to one tonne of raw hides

Description	Average
Applied in curing	400 kg
Discharged as leachate resulting from dehydration of raw hides	60 kg
Fallen during handling and transport of raw stock	40 kg
Fallen during trimming, cutting into sides, handling, etc in the raw material store (This is generally collected for safe disposal or reuse)	15 kg
Removed during mechanical desalting – 12.5% (of applied salt)*	50 kg
Removed during manual desalting using DODECA frame – 20% (of applied salt)#	80 kg
Washed out in 1st soak – 300% float	120-145 kg
Washed out in 2nd soak liquor – 300% float	45-60 kg
Carried over by hides to further operations (estimate)	30-40 kg



CHLORIDES Cl^-

Sodium chloride is normally introduced into effluent through the large amount of common salt used to both preserve and pickle hides and skins. Based on findings from a number of tests carried out under a UNIDO supported project in India, *Figure 2* shows what happens to the salt applied in preservation.

SULFATES (SO_4^{2-})

The source of sulfates includes sulfuric acid, chrome tanning and retanning salts, specialty products with a high sodium sulfate content, and many dyestuffs. An additional source stems from the oxidation of sulphides in the effluent treatment plants: first to thiosulfate during catalytic oxidation in primary treatment, and ultimately into sulfate during biological treatment.

No single solution to salinity

There is no one-track solution. The problem has to be attacked on a wide front covering hide and skins preservation, processing, and end-of-pipe treatment. Different methods need combining simultaneously, including:

AVOIDANCE OF COMMON SALT IN CURING

Curing by drying: Frame-drying and suspension drying. This is labour-intensive and time-consuming. Natural drying is not applicable in cold countries.

Curing by cooling and chilling: Only suitable where abattoirs, rawhide depots, transport vehicles and tanneries have the requisite refrigeration and transport facilities. Very energy-intensive

Dry salting: The salt requirements are halved, but the technique is labour-intensive and time-consuming.

Other salt-free curing options: Electron beam irradiation, Liricure method, use of antiseptics and preservatives as a complementary treatment.

In-plant desalting techniques

THE PERFORATED DRUM

About 5-6% of salt on raw stock weight can be removed by tumbling in a perforated drum. In other words, about 15% of salt from curing retained by hides can be removed and recovered by this method. The method is low cost and appropriate for large hides or a large quantity of skins.

BRUSH-TYPE RESALTING MACHINE

The desalting machine is fitted with a cylindrical roller embedded with hard nylon bristles in a helical pattern. This is available in different working widths, and has an operating capacity about 100 wet salted bovine hides/hour. It is a low cost option.

MANUAL DESALTING

Manual desalting is useful in low labour cost countries. Tanneries processing goat/sheepskins or cow/buff calfskins desalt by hand brushing. This can be reasonably effective.

Alternatively, raw stock can be beaten three times on a wooden stool with a dome-like top frame known as a DODECA frame, shown as *Figure 3*. Four workers are needed to desalt hides, and



Figure 3: The Dodeca frame

two for smaller hides and skins. It takes about 2 hours to desalt a tonne of raw stock.

While the quantity of salt removed varies with the method of desalting, it is generally in the range of 4-8% on the weight of raw stock taken for desalting. Although there are many impurities, a fairly clear solution can be obtained by dissolving the recovered salt, simple screening, and then clarification

using poly-aluminium chloride. Demonstrations showed that the salt solution so obtained could be safely used in pickling operations.

When these techniques are used the TDS level in the composite tannery wastewater are reduced by about 15%. In practice the TDS in the composite effluent of a tannery processing salted raw hides/skins to semi-finished leather is reduced from 12,000-18,000 mg/l to 10,500-15,700 mg/l.

Modifications to traditional wet processing

Considerable reduction of TDS can be achieved by recycling certain floats, ammonium sulphate-free deliming and bating, low-salt pickling, appropriate chrome management system etc.

The segregation of saline waste floats

In the state of Tamil Nadu, India, very saline streams (soak and pickling streams) have been segregated, then concentrated by evaporation in outdoor solar pans. The results were rather disappointing due to low evaporation rates in a humid climate, rainy periods, large areas required, and the presence of dirt and impurities. Improvements have been achieved by accelerating the evaporation rate using a grid of fine nozzle sprinklers.

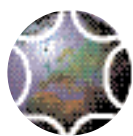
Membrane technology: permeates and concentrates

The tests have been carried out under a UNIDO supported project in India using an industrial pilot plant of capacity about 1 m³/hour. This proved the technical viability of using membrane (reverse osmosis) technology to drastically reduce the TDS in a well-treated tannery effluent.

The TDS values of the effluent taken for treatment ranged from about 3,000 to 8,300 mg/l (average 5,100 mg/l) and chlorides from 810 to 2,620 mg/l (average 1,215 mg/l). The rate of recovery of permeate with an average TDS value of less than 500 mg/l, was 70-75%.

However, the cost of treatment was \$0.76/ m³ (not including depreciation or cost of capital.) This is more than the price paid for fresh water brought from unpolluted areas (\$0.67/m³). Even assuming that the cost of treatment in an industrial scale system would be somewhat lower than in the pilot plant, there still remains the problem of disposal of the 25-30% concentrate containing all of the separated salt. The conclusion is that this is not a promising avenue.

Reverse osmosis was rejected in the Santa Croce sull'Arno region in Italy. This was due to unacceptable investment and operation costs, and difficulties with disposal of the concentrate. In this situation the concentrate was estimated at 15-20% of the original volume, and the sea about 50 km from the area.



Reuse of treated effluent for irrigation

Under a UNIDO supported project in India a “mini-forest” was set up on a 3.5 ha plot of barren land. About 800 m³/day of treated effluent emanating from tanneries processing wet blue leathers, having a TDS <4500 mg/l, chlorides of <900 mg/l was used for irrigation. Salinity resistant species of trees (*including: Casuarina equisetifolia, Acacia mangium, Eucalyptus tereticornis and Azadirachta indica*) were selected and given appropriate adjustment time. Soil and ground water characteristics were continuously monitored for any signs of deterioration.

The success of the experiment has to be interpreted and possibly replicated with great caution. The balance between the salt load, volume as effluent and rainwater, and evaporation and salinity in ground water needs special attention. A way forward, but applicable to only specific situations.

Relocation of tanneries or discharge of saline waters into the sea

While the relocation of existing tanneries is unlikely, it is reasonable to expect that the problem of TDS in effluent will play a significant role in site selection for new plants. Similarly, construction of pipelines taking saline effluents to the sea will be limited to very few tannery clusters.

Combined treatment of tannery and municipal wastewaters

There are considerable differences in the characteristics of municipal (sewage) wastewaters. In particular, the content of chlorides and sulphates does not exceed 1000 and 400 mg/l respectively, and in most cases is much lower. This is low in comparison with tannery effluents, but sewage wastewaters are high on phosphates, and these are needed for biological treatment. Combined treatment of pre-treated tannery effluents and municipal wastewaters is therefore very desirable.

This has been recognised in the S. Croce sull'Arno tannery region where the entire system of several separate tannery and sewage treatment plants is supposed to be “restructured”.

In this event the following details need taking into account:

- collect and treat all industrial/tannery effluents at only one centralised plant (AQUARNO)
- collect and treat domestic wastewaters from the whole region at one plant (CUOIODEPUR.) Part of the treated effluent for (re)use in tanneries, a new network construction being required for this purpose
- merge the rest of the domestic wastewaters with treated tannery effluents from AQUARNO. After final biological treatment, discharge into the Arno river.

Evidently, the ratio of industrial vs. sewage wastewater is crucial. The ultimately goal is a ratio 1:5, and the main benefits expected from these plans are:

- lower overall operation costs
- conformity with discharge limits for chlorides and sulphates (or at least come close to it)
- avoidance of very expensive tertiary treatment of tannery effluents
- reduced pressure on rapidly depleting sources of the ground water.

Panel I

Pollution limits for TDS, Chloride and Sulfate: surface and sewer discharge in selected countries

		TDS	Cl-	(SO ₄) ²⁻
India	A	2100	1000	1000
	B	-	-	1000
Italy [†]	A	-	1200	1000
	B	-	1200	1000
Spain	A	-	2000	2000
	B	-	2000	2000
UK	A	-	4000	-
	B	-	5000	1200
Zimbabwe	A	-	1000	1000
	B	-	4000	300
USA	A	-	-	-
	B	-	-	-
Argentina	A	-	*	*
	B	-	*	1000
Germany	A	-		
	B	-		

A: Surface B: Sewer * Specific requirements have to be met.

[†] Special limits permitted by the regional authorities for some CETPs located close to the sea or if mixed with sanitary wastewater: -

- In Santa Croce, Cuoidepur and Fuccechio: chlorides – 5,000 mg/l; sulphates – 1,800 mg/l
- In Arzignano: chlorides – 2,900 mg/l; sulphates – 1,800 mg/l
- In Solofra: chlorides – 3,500 mg/l; sulphates – 1,500 mg/l

The only way forward

Conventional and affordable tannery effluent treatment systems do not reduce the chloride and sulphates content. Consequently, treated effluents from tanneries processing salted raw material remain potentially hazardous to the environment, especially to water resources in arid regions.

Various in-plant methods can be used for prevention, and some end-of-pipe methods can help reduce the impact of saline effluent. However, to date results fall short of legal requirements or are applicable only under specific local conditions.

The only feasible approach appears to be a combination of reduction of load at source and rationalised treatment, that is:

- salt-free curing
- combined treatment of tannery and sewage wastewaters.

For reasons not necessarily directly associated with the problem of salinity, this situation already prevails in many industrialised countries.

In contrast, in most developing countries it remains a long-term perspective. Sewage systems are a rarity, and inadequate abattoir and transport facilities do not allow the processing of fresh hides and skins. Furthermore, preservation by drying is seen as a backward step to both raw material dealers and tanners. Clean, effective and low cost alternatives to salting are badly needed.